Low-temperature properties and localized electronic states of glasses

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The basic ideas and a number of results of the theory of low-energy excitations and localized electronic states, which are responsible for the universal low-temperature anomalies in glasses and unusual electronic properties of nonmetallic glasses, primarily glassy semiconductors, are reviewed. The basic hypotheses and models, previously proposed in this connection in order to explain the numerous empirical data, are discussed. Recently developed concepts regarding soft atomic configurations as a significant feature of the structure of glasses, determining new types of low-energy excitations in such anharmonic systems and of localized electronic states—self-trapped electron pairs with negative correlation energy, with very strong interelectronic attraction—are examined. The above-mentioned properties of glasses are analyzed on the basis of this theory and briefly compared with experiment. Some important problems in the theory of glasses are indicated.

CONTENTS

1. INTRODUCTION

During the last decade glasses and glassy materials, as well as some other amorphous systems, have become an object of intensive experimental and theoretical study.[1–3] Glass is customarily classified as an amorphous solid, which is prepared in the form of a massive sample during the cooling of the melt at a sufficiently high rate $q \geqslant q_g$ to some characteristic vitrification temperature $\theta(q) \geqslant \theta(q_g) \equiv T_g$, appreciably lower than the crystallization temperature T_f (often $T_g \approx 2T_f/3$). Since the crystal is thermodynamically stable at temperatures $T < T_f$, the glass, which exists at temperatures $T < T_g$, is a nonequilibrium metastable system, whose lifetime t_L, however, is macroscopically long.

Glasses, like other amorphous materials, are characterized by a definite short-range order with no topological order.[1] Topological disorder corresponds not only to the absence of crystalline long-range order, but also to the fact that the topological properties cannot be reduced to those of a real crystal.[1,6] Short-range order for an atom A_i of a given type ($i = 1, 2, \ldots$) is usually characterized by a definite number of nearest neighbors (coordination number) z_i and a pair distribution function $\rho_i^{(1)}(R)$ for these neighbors, with a fixed "average" relative arrangement of the neighbors, at distances of the order of the average interatomic distance $a_1 \approx 3$ Å. Experimental methods (x-ray, neutron, etc.) for studying the structure of glass usually give information about the short-range order—truncated, "one-dimensional" version of the real three- (or two-) dimensional amorphous structure.[1] However the presence of "intermediate" range order over distances of the order of $a_2 \approx 10$ Å is being increasingly observed experimentally.

The properties of glasses are in many ways anomalous both at high temperatures $T \approx T_g$ and low temperatures $T \ll \hbar\omega_D$, in the sense that they have no analogs in standard crystals. At the same time at temperatures $T \ll \hbar\omega_D$ some similar anomalies have been found in superionic conductors and specific crystals, including crystals containing high concentrations of defects of the off-center type or radiation-induced disordered regions (see, for example, Refs. 1, 4, 5, and 31). The models most widely employed for describing the structure of glasses are apparently the model of a "continuous random network" (CRN) of atoms connected by covalent bonds and the related model of "random close packing" (RCP) of atoms. The CRN model is often employed to describe the structure of amorphous silicon (a-Si) and chalcogenide glasses (a-$C_{1-x}Q_x$ where C≡Se, Te and Q≡P, As, Sb, Ge, Si, where $0 \leqslant x \lesssim 0.5$–$0.6$), while the RCP model is employed for describing metallic glasses, i.e., the amorphous alloys M_xQ_{1-x} with $x \approx 0.7$–0.8 (M is a transition metal and Q≡Ge, Si, P, B, and others). Such models actually take

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only the short-range order into account and are microscopically uniform. At the same time they address the large disorder, the significant fluctuations in the numbers ν of atoms in separate structural units from even (average) values $\nu_0 = 2k$ ($k = 1, 2, \ldots$) characteristic for crystals, and the significant relative fraction ($\approx 30\%$) of the corresponding local atomic configurations for which symmetry axes of odd $(2k+1)$ order (fifth and seventh orders with $\nu_0 = 6$), which are not encountered in ideal crystals (but are typical for quasicrystals; see, for example, Ref. 130), are characteristic.

On the other hand, less disordered, but microscopically more nonuniform models are under discussion. Thus in the model of Ref. 7 the glass looks more like a multibond system of atomic clusters with dimensions of $\approx a_3 \approx 30$–100 Å, containing smaller clusters of size $\approx a_2 \approx 10$–15 Å. In such models the intermediate order can be taken into account, while the universality of the anomalous properties is correlated with that of the structure of the overall "inner surface" of this complicated system of clusters.[7,8] Another model of glass, essentially a thermodynamic model, attributes the anomalous properties of the glass to the existence of "free volume" $v_f \equiv v - v_0^*$ largely in the form of voids with a size of $\approx a_1^3$, near which significant motions of atoms occur (v is the random volume per atom and v_0^* is its characteristic value, close to that of the crystal; $v_0^* \approx a_1^3$).[9] In models of the CRN type or cluster models the distribution of the excess volume of the glass, compared with the crystalline distribution, can be more complicated.

The enormous number of different glasses can be divided into three basic classes according to the width E_{opt} of the main optical gap: 1) dielectric glasses, including oxide ones (a-SiO_2, etc.), with a more or less significant relative fraction of ionic bonds and very large gap width $E_{opt} \approx 5$–10 eV; 2) glassy semiconductors, including chalcogenide semiconductors, with predominantly covalent bonds and a moderately large gap width $E_{opt} \approx 1$–3 eV; and, 3) metallic glasses (no optical gap).

This review is devoted to a discussion of the present status of the theory of anomalous (in the sense indicated above) properties of glass far from the vitrification temperature T_g ($T \lesssim T_g/2$). The following are primarily discussed: 1) low-temperature ($T \ll \hbar\omega_D$) properties of nonmetallic glasses (Secs. 2 and 3)[1)] and 2) electronic phenomena in glassy semiconductors (GS) at temperatures $T \lesssim T_g/2$ (Secs. 4 and 5). Because the length of this article is limited we shall talk primarily about recently developed concepts and the theory of low-energy excitations and localized electronic states in glasses based on them. The main experimental facts and earlier models proposed to interpret them are discussed very briefly, in particular, because they are examined in detail in a number of reviews cited below. In addition, the references cited for this review are unavoidably only representative and not exhaustive.

2. LOW-TEMPERATURE PHENOMENA IN GLASSES

2.1. Basic experimental facts

The anomalous (in the sense indicated above) behavior of the basic properties of glasses (g) at low temperatures $T \ll \hbar\omega_D$ (see, for example, Refs. 10–12) can be illustrated on the example of the heat capacity $C_g(T)$ and the phonon thermal conductivity $\chi_g(T)$. The values of C_g and χ_g at a fixed temperature T are respectively significantly higher $C_g \gg C_0^{(D)}$ and lower $\chi_g \ll \chi_0^{(ph)}$ than in the corresponding crystals (0). At the same time (Fig. 1),[3,11,12] at least for temperatures $T \lesssim 30$ K,

$$\Delta C_g \equiv C_g - C_g^{(D)} \approx \beta_g T^{1+n} + \alpha_g(T)\, T^3, \quad 0 \leqslant n \leqslant 0.3, \tag{2.1}$$

$$\chi_g \approx \gamma_g T^{2-m}, \quad 0 \leqslant m \leqslant 0.25, \text{ for } T \leqslant 1 \text{ K}, \tag{2.2}$$

or $\chi_g \approx$ const ("plateau") at moderate temperatures $5 \lesssim T \lesssim 30$ K, where $\alpha_g(T)$ has a broad maximum ("hump"). Outside the last interval $\alpha_g(T) \approx \alpha_g^0 \approx \text{const} \gtrsim \alpha_g^{(D)}$, exceeding the Debye coefficient, determined from the measurement of the velocity of sound, $\alpha_g^{(D)} \approx C_g^{(D)}/T^3 (\gtrsim C_0^{(D)}/T^3)$. At higher temperatures $T(\lesssim \hbar\omega_D/2)$ both C_g and χ_g are observed to increase as T increases.[3] Variations of the coefficients β_g and γ_g for all the great variety of glasses studied are unexpectedly small, $\beta_g^{-1} \approx 30$–$100\ \text{eV}^{1+n}$ and $\gamma_g \approx 10^{-4}$–$10^{-3}\ \text{W}\cdot\text{K}^m\cdot\text{cm}^{-1}$. It is also interesting that β_g and γ_g depend on T_g (see, for example, Refs. 31–33).

In glasses the phonon or photon mean-free path lengths $l_{ph}(\omega, T)$, the coefficient of absorption $\alpha_{ac,em}(\omega, T)$ of a weak acoustic (ac) or electromagnetic (em) wave, and other acoustic and dielectric characteristics as well as nonlinear phenomena (suppression of the absorption of a wave with increasing intensity of the wave, effects of the echo type, etc.), somewhat reminiscent of those occurring in spin systems at very low temperatures $T \lesssim 1$ K (see, for example, Refs. 3, 11–14), also exhibit anomalous behavior.

Three basic features of the low-temperature properties of glasses can be distinguished[3]: 1) anomalousness; 2) universality; and, 3) characteristic nature, i.e., the main contribution does not depend on the impurities (for example, He atoms in a-SiO_2).

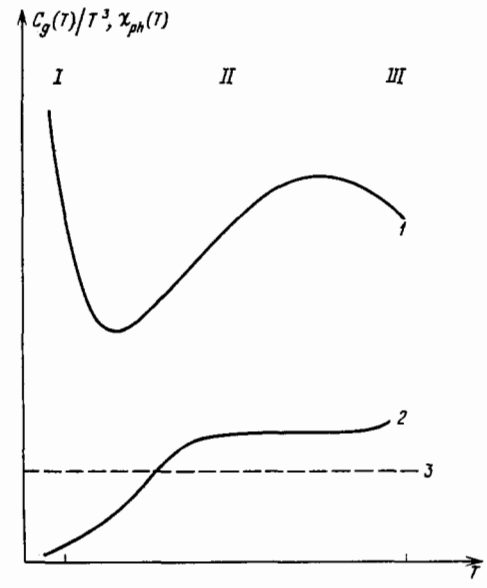

FIG. 1. Schematic diagram of the empirical temperature dependence of the reduced heat capacity $C_g(T)/T^3$ (curve 1) and phonon thermal conductivity (2) of glass at low temperatures $T \ll \hbar\omega_D$.[3] Curve 3 corresponds to the usually expected Debye heat capacity for the empirical velocity of sound (the relation between the curves 1 and 3 is typical, while here the relationship between curves 1 and 2 is not). There are three clearly defined regions of T: I) $T \lesssim 1$ K; II) $5 \lesssim T \lesssim 30$ K; III) higher temperatures $T(\ll \hbar\omega_D)$.

2.2. Tunneling model

The phenomenological tunneling model, used for interpreting the above-mentioned and other anomalous properties of glasses, is based on two hypotheses[15,16]:

I. There exists in the glass a finite concentration $c^{(2)}$ ($\ll 1$) of "atoms" (separate atoms or small groups of atoms), to each of which there corresponds not one (as usual in a crystal), but rather two positions of equilibrium, close both in energy (E_0, E_1), $\mathscr{E} \equiv E_1 - E_0 = 2(\Delta^2 + J^2)^{1/2} \ll \hbar\omega_0$, and spatially ($|x_1 - x_2| \equiv l < a_D$), i.e., a two-well potential with the bottom of both wells differing in energy by $2\Delta \ll \hbar\omega_0$ and a tunneling amplitude $J = \hbar\omega_0 \exp(-\lambda) \ll h\omega_0$, where ω_0 is the characteristic frequency of intrawell oscillations.

II. The density of the distribution of the random values of ω_0, the mass of an "atom" M, and the interwell distance l is narrow ($\omega_0 \approx \omega_D$, $M \approx$ const, $l \approx$ const $< a_1$), but uniform for statistically independent Δ and $\lambda = c_0 l (2MV_B)^{1/2} \times (c_0 \sim 1)$:

$$P(\Delta, \lambda) \approx P_0 = \text{const for } 0 \leqslant \Delta \leqslant \Delta_{\max} \text{ and } \lambda_{\max} > \lambda > \lambda_{\min} (>1), \tag{2.3}$$

and in addition it is often actually assumed that the heights of the barriers satisfy $V_B \leqslant V_{\max} (<\infty)$ and $\Delta_{\max} \lesssim V_{\max}$, while $\lambda_{\max} \equiv \lambda(V_{\max}) \gg 1$ for $V_{\max} \gtrsim T_g$ (see Refs. 2, 15, and 16). In this model the main low-energy excitations $\mathscr{E} \ll \hbar\omega_D$ are "two-level systems" (TLS), corresponding to the splitting of the ground level of the potential well into close levels E_0 and E_1 owing to weak atomic tunneling and asymmetry of the two-well potential and in many respects being analogs of spin 1/2. As usual, two types of interactions of TLS with acoustic and electromagnetic waves with frequency ω are distinguished: 1) resonance interactions for $\hbar\omega = \mathscr{E}$ and 2) relaxational interactions, arising with modulations of the levels of the TLS of the population of the levels, and relaxation of the population (see Refs. 11–16). In different regions of values of $\mathscr{E}$ ($\ll \hbar\omega_D$), T ($\ll \hbar\omega_D$) and other parameters of the material the resonance or relaxational processes can dominate, and the relaxational processes can be single-phonon (for $T < \theta_0 \sim 10$ K $\ll \hbar\omega_D$) or they can include a large number of phonons (for $T > \theta_0$).[11,12,18–23,29] An important prediction of the model is that a dependence of the nonresonant phenomena, determined by the contribution of TLS, on the duration of the experiment t_e is established. This dependence is brought about by the very large spread in the values of the amplitude $J(\lambda)$ and relaxation time $\tau(\mathscr{E}, J) \propto J^{-2}$, so that both values $\tau < t_e$ and $\tau > t_e$ can be encountered, and only TLS with $\tau \lesssim t_e$ contribute to the real phenomena.[15]

The most important consequences of the model are the following: 1) the TLS contribute to the heat capacity $C_{TLS}(T, t_e) \propto T\varphi(t_e)$, where $\varphi(t_e) \propto \ln t_e$ for $t_e < \tau_{\max}$ or $\varphi(t_e) \approx$ const for $t_e > \tau_{\max}$, where $\tau_{\max}$ is the longest relaxation time of the TLS (finite for $\lambda \approx \lambda_{\max} < \infty$), and 2) resonance scattering of the thermal acoustic phonons by TLS contributes to the thermal conductivity $\chi_g \sim T^2$.[11–16] The model can qualitatively interpret a number of phenomena in glasses at temperatures $T \lesssim 1$ K, including nonlinear effects of the echo type, determined, by analogy to spin systems, by the longitudinal and transverse (owing to the interaction between TLS "spins") relaxation.[11,12,14,18,24–27] This analogy, however, is limited: transverse relaxation also occurs for separate TLS.[28]

Comparison of the formulas and estimates obtained in the tunneling model with the corresponding experimental data (for temperatures $T \lesssim 1$ K) gives the following values for the basic parameters of the model[3,11,12,31]:

$$P_0 \approx 10^{19} - 10^{20} \text{ cm}^{-3} \text{ eV}^{-1} \text{ and } |\bar{b}_1| \approx 0.3 - 1 \text{ eV}, \tag{2.4}$$

where $\bar{b}_1$ is the characteristic coupling parameter of the TLS with the low-frequency acoustic phonons ($\omega \ll \omega_D$). At the same time for a concentration c_{TLS} (ξ_0) of TLS with energies $\mathscr{E} \leqslant \mathscr{E}_0$ it turns out that $c_{TLS}(\mathscr{E}_0 = 1 \text{ K}) \approx 10^{-5}$–$10^{-6}$.

In recent years different macroscopic structural models of TLS in glasses, the relations between which are by no means understood, have also been proposed (see Refs. 7, 9, 32–38, 46, and 47).

2.3. Problems of the tunneling model

The tunneling model, however, has a number of problems, including the following basic ones (see Refs. 2 and 8): 1) what is the general nature of the tunneling "atoms" and why are there so many of them, $c_{TLS}(\mathscr{E}_0 = 1 \text{ K}) \approx 10^{-5}$; 2) why is $P(\Delta, \lambda)$ uniform over Δ and especially over λ; 3) why is the TLS-phonon coupling so strong that $|\bar{b}_1| \gg \hbar\omega_D$; 4) why, as proposed additionally in Ref. 18, a) are there two types of TLS and b) do the values of $|\bar{b}_1|$ for them differ significantly; 5) what is the nature and properties of excitations with moderately low energies $\mathscr{E} \approx 5$–30 K, determining phenomena in glasses at temperatures $T \approx 5$–30 K, and how are they related to the tunneling TLS (see also Refs. 20, 30, and 45)?

In the structural TLS models mentioned above only the first problem and in part, the second problem are actually discussed, but there are no estimates of P_0 and $\bar{b}_1$, and the problems 3)–5) are essentially not studied.

Thus the tunneling model and the above-mentioned structural TLS models have led to a number of achievements in the qualitative interpretation of the experimental data and some predictions (dependence of C_g on t_e) as well as to significant problems. The existence of the problems obviously indicates that the structure of low-energy excitations in glasses is more complicated than assumed in the tunneling model and its modifications.

3. LOW-ENERGY EXCITATIONS AND PHENOMENA IN GLASSES

In this section the theory of low-energy excitations of the atomic subsystem of a glass, differing substantially from TLS in "rigid" two-well potentials (TWP) ($\omega_0 \approx \omega_D$) and also from phonons, is reviewed. This theory, having essentially a microscopic basis and not directly related with the specific model of the structure of the glass, is the key and actually leads, to a large extent, to the solution of the above-mentioned problems and analysis of the basic low-temperature properties of glasses, at least for temperatures $T \lesssim 30$ K.[8,39,40]

The theory is based on the model of soft atomic local configurations, the soft configurations being regarded as a fundamental component of the structure of the glass. Some of the structural TLS models mentioned above, like the tun-

neling model, may turn out to be particular cases of the model of soft configurations.

3.1. Model of soft atomic configurations and critical potentials

In an amorphous system there exist such large (though rare) fluctuations of the parameters of the local atomic configurations and deviations from their average values, corresponding to the short-range order, that in each such configuration the motion of some "atom" (separate atom or small group of atoms) along a definite coordinate x occurs in a local potential $V(x)$ with an anomalously small quasielastic parameter $|k(x)| \equiv |d^2V(x)/dx^2| \ll k^{(0)} \equiv M\omega_D^2 \sim 30$ eV/Å^2. The local potential $V(x)$, characterizing the change in the potential energy of the entire system in a multidimensional configuration space accompanying the displacement of an "atom" x in a small region $\Delta x \lesssim a_0 \approx 1$ Å and fixed values of all other atomic coordinates, can be characterized not only by values of $k(x) > 0$, as happens, in particular, near the minima of potentials ($k \equiv k(x_{\min}) > 0$), but also by $k(x) < 0$ for values of x corresponding to unstable configurations near an "atom." The latter indicates that the local potential $V(x)$ is not a single-well potential and has at least one maximum near which $k(x_{\max}) < 0$. The local configuration near such an "atom," for $|k(x)| \ll k^{(0)}$, can be restructured comparatively easily with a significant displacement $|x| \lesssim a_0$, and in this sense it is soft, while the "atom" itself is bound quite weakly with the surrounding configuration. In other words, such a local configuration is close to being unstable, and small changes in its parameters give rise to a significant change in the position and form of the local potential of a weakly bound "atom." The local potentials under study, called in this connection critical, are strongly anharmonic and are thereby distinguished from the usual type of harmonic single-well atomic potentials. The latter correspond to most atoms in an amorphous system, and only a small fraction $c_a \ll 1$ of the atoms is characterized by the unusual, critical, potentials. On the basis of this theory glasses are amorphous systems in which c_a assumes its highest value, reaching a limiting value comparable to the solid state, $c_a = (c_a)_{\max}$ (in an ideal crystal $c_a \approx 0$). In this sense glasses are solids with a significant anharmonicity of the bonds. As demonstrated in this theory,[8,39–41] the typical, most likely critical potentials, realized for a small fraction $c_a \ll 1$ of atoms, are characteristic only for one of the modes of the motion of the "atom," its "critical," slow ($|k(x)| \ll k^0$) mode x (the faster motions of the atom and other atoms for $k \approx k^{(0)}$ are averaged over time, leading only to a constant renormalization of the parameters of the critical mode; see Sec. 3.3). The formula describing the critical potential is approximated here by the expression[8,40]

$$V(x) \approx A(\eta x^2 + \xi x^3 + x^4) \quad \text{for} \quad |\eta| \ll 1 \text{ and } \xi^2 \ll 1, \tag{3.1}$$

adequate in practice for actual, not too large displacements $|x| \lesssim 1$ of the "atom"; this can be verified in an obvious manner in specific models. For the other modes the atomic potential, as usual, is "rigid" ($k \approx k^{(0)}$), single-well, and harmonic. The coordinate x of the critical mode is scaled to the atomic unit of length a_0 (≈ 1 Å), and it is assumed that $V(0) \equiv 0$ and $x \equiv 0$ for one of the extrema of the local potential; $A \equiv (1/2)k^{(0)}a_0^2 \sim 30$ eV and $k^{(0)} \equiv M\omega_D^2$ are the standard scales of the elastic energy and atomic quasielastic constant; $\eta \lesseqgtr 0$ and $\xi \lesseqgtr 0$ are the basic random parameters of the local configurations in the amorphous system. Obviously, ξ characterizes the asymmetry of the potential with respect to the critical mode, whose typical (most probable) values are small, $\xi^2 \ll 1$, in agreement with the condition of mechanical stability (see Refs. 8 and 40). Similar single-mode expressions describe the behavior near the critical point of the thermodynamic potential in the theory of thermodynamic phase transitions[42] and some general characteristics of the system in the mathematical "theory of catastrophies."[43]

The main characteristic of the structure of glass in this model is the density of the distribution of configurational parameters $F(\eta,\xi) = F(\eta, -\xi)$, which gives a "two-dimensional" description of the structure [compare $\rho_i(R)$ in Sec. 1]. Generally speaking $F(\eta,\xi)$ must have a maximum near $\eta = \bar{\eta} \approx 1$ and $\xi = \bar{\xi}$ for $\bar{\xi} = 0$ or $\bar{\xi} = \pm\xi_0, \xi^2 \ll 1$, for most atoms in the usual "rigid" ($k \approx k^{(0)}$) single-well harmonic potentials, including potentials of the type $V(x) \approx Ax^2$, corresponding to the extrapolation of (3.1) into the region $\eta \sim 1$ (Fig. 2). The rapidly (but not necessarily monotonically) decreasing "tail" of $F(\eta,\xi)$ on the η axis for $\eta_0^* \bar{\eta}$ corresponds at first to the critical potentials ($k \ll k^{(0)}$) for $|\eta| \ll 1$, and then in the more distant region for $\eta < 0$ and $|\eta| \gtrsim 1$ to the "rigid" two-well potentials with $k \approx k^{(0)}$ in each well (see discussion below).

Local atomic potentials are characterized here by the number of wells and the spectrum of the random values of the intrawell quasielastic constants $k \equiv k(x_{\min})$, $0 \leqslant k \lesssim k^{(0)}$, with the probability density distribution $G(k)$ of the type

$$G(Q) = \int\int F(\eta, \xi)\, \delta(Q - Q(\eta, \xi))\, d\eta\, d\xi. \tag{3.2}$$

The expressions for $k(\eta,\xi)$ have the form[8,41]

$$k = k_0 \equiv k(x_0 \equiv 0) = k^{(0)}\eta \ll k^{(0)}$$

$$\text{for} \quad \eta^{(0)} \equiv \frac{9\xi^2}{32} < \eta \ll 1; \tag{3.3}$$

$$k = k_{1,2} \equiv k(x_{1,2}) = 2k^{(0)}\eta^{(0)}(\Lambda \mp \Lambda^{1/2}), \tag{3.4}$$

$$\Lambda \equiv 1 - \frac{\eta}{\eta^0} \quad \text{for} \quad |\eta| = -\eta \ll 1,$$

or

$$k = k_0' \ll k^{(0)}, \quad k = k_2 \ll k^{(0)} \quad \text{for} \quad 0 < \eta < \eta^{(0)} \ll 1 \tag{3.5}$$

correspondingly for critical single-well potentials for $x_{\min} = x_0 \equiv 0$, as well as critical two-well and "singular" potentials for $x_{\min} = x_{1,2} = (3\xi/8)(-1 \pm \Lambda^{1/2})$ ($j = 1$) or $x_{\min} \equiv \{x_0, x_2\}$ ($j = 2$). At the same time in the (η,ξ) plane it is possible to separate two lines of critical points,

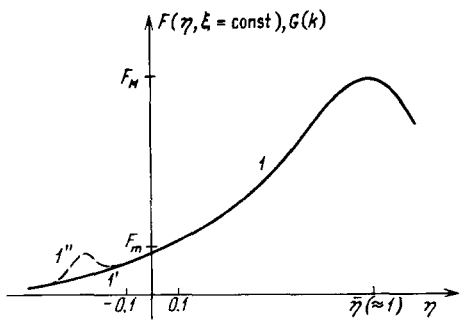

FIG. 2. General possible forms of the function $F(\eta,\xi = \text{const})$ (the case with $F_0^* \equiv F(0,\bar{\xi}) \neq 0$)[8] (compare Ref. 124). 1') Monotonic behavior or 1'') nonmonotonic behavior (for $F_M \equiv F(\eta) \gg F_0 \gtrsim F_m \equiv F(\eta_m) \geqslant F_0^*$).

$k(\eta,\xi) = 0$, separating three classes of critical potentials: 1) single-well (CSW); 2) two-well with an appreciable interwell barrier (CTW) of two types: near $\xi = 0$ for $\eta < 0 (j = 1)$ and near $\eta = \xi^2/4$ for $0 < \eta < \eta^{(0)} (j = 2)$; and, 3) "singular" (CSP) near both lines of critical points.

We point out in this connection the following: the form of the separate potential wells and interwell barrier for CTW, though different for different values of η and ξ, approaches the harmonic form as $|\eta| (j = 1)$ or $\xi^2 (j = 2)$ increase; the singular potentials here can be regarded as "intermediate" in the sense that they are similar to CTW with a vanishing barrier or CSW with an inflection point; the physical characteristics of the critical potentials, differing from the single-well potentials (i.e., CTW and CSP), are translationally invariant: the values and forms of the dependences for them do not change under a translation of the origin of the coordinate system from one extremum to another.

The relationship between this general model and the specific model of the structure of the glass (including one of the models noted above in Secs. 1 and 2c), described by random configurations of the parameters Y and their distribution $\rho(Y)$, is determined, as soon as the explicit form of the functions $\eta(Y)$ and $\xi(Y)$, the mode x, as well as the function $F(\eta,\xi) = \int dY\rho(Y)\delta\eta - \eta(Y)\delta(\xi - \xi(Y)$ have been found. In particular, Y can be the angles between the covalent bonds and/or between the faces of neighboring elementary polyhedra of the amorphous structure (see Refs. 1 and 41). In the general case, however, the existence of soft configurations as a possible component of the structure of the glass (g) must be related with the excess, compared with the crystalline (0), average volume v_a per atom $\delta v_a = v_a - v_0 > 0$, i.e., by a deficit of the (average) density $\delta\bar{\rho}_a = \bar{\rho}_a - \rho_0 < 0$, whose magnitude is highest in glasses, $|\delta\bar{\rho}_g| \sim 0.1\rho_0$ (the relationship between the breakdown in long-range order in a crystal as the volume increases with $T = \text{const}$ and the appearance of multiwell potentials was first pointed out in Ref. 44 in an analysis of melting). In this connection it may be assumed that the expression

$$\eta = \nu (v_c - v) \equiv \Omega_c - \Omega, \quad \nu = \text{const} \sim 1, \tag{3.6}$$

is of a quite general character; here v is the random volume per atom, scaled to the atomic volume a_0^d ($d = 3$ or 2), and v_c is its critical value characteristic for the material, and a mode of the "compression-expansion" type is the critical mode. For a critical mode of a different type (shear, rotational, etc.) η and ξ have a different microscopic meaning. The simplest model of the type (3.6) (Fig. 3), in which the local configuration is a fragment of a chain including the "atom" (0) and the nearest neighbors (-1, 1), with some angle θ between the bonds, has been studied in a number of articles.[8,40,41,45] In this model both the standard "rigid" and anomalous, critical atomic potentials are determined directly, while the function $F(\eta,\xi)$ can be expressed directly in terms of the radial distribution function for the second nearest neighbors in the glass.

The concentrations (relative fractions) of atoms in single-well ($c_a^{(1)}$), two-well ($c_a^{(2)}$) and singular ($c_a^{(3)}$) critical potentials are determined by the function $F(\eta,\xi)$ in expressions of the type

$$c_a^{(1)} = \int d\xi \int_{\eta^{(0)}}^{\eta^*} d\eta F(\eta, \xi),$$

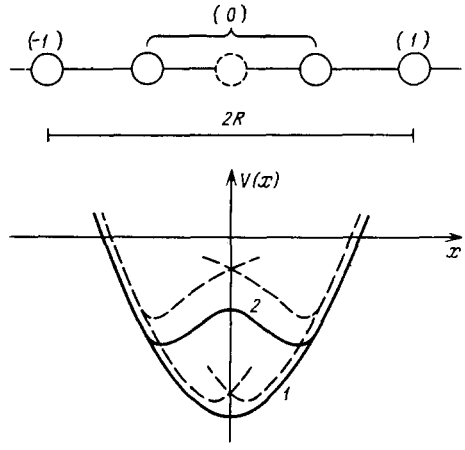

FIG. 3. Three-atom fragment: potential energy of the system relative to the displacement of the atom (0)—single-well (1) or two-well (2).[8,41]

$$c_0^{(2)} = \sum_{j=1,2} \int \int_{\eta_{1j}^{(r)}}^{\eta_{2j}^{(r)}} F(\eta, \xi)\, d\eta\, d\xi \quad (r = 2, 3) \tag{3.7}$$

for

$$\int\int F(\eta, \xi)\, d\eta\, d\xi = 1, \quad c_a = \sum_{r=1}^{3} c_a^{(r)} \ll 1.$$

Here the parameter $\eta^* \ll 1$ depends slightly on the phenomenon under study, and the typical values $\eta^* \approx 0.1$–0.3; $\eta_{1j}^{(r)}$ can be found from the definition of both ($j = 1,2$) types of CTW ($r = 2$) and CSP ($r = 3$), for example, $\eta_{11}^{(2)} \approx -\eta^*$ and $\eta_{21}^{(2)} \approx 0$. The empirical smallness of $c_a^{(2)}$ [$> c_{TLS}$; see (2.4)] corresponds to the smallness of the scales η_c and $\xi_c \equiv (32\eta_c^{(0)}/9)^{1/2}$ for the decay of $F(\eta,\xi)$ on the η axis for $|\eta| \ll 1$ and on the ξ axis $\eta^{(0)}, \eta_c \ll 1$ and $\eta_c^{(0)} \ll 1$. Using the approximation, valid in some specific models,

$$F(\eta, \xi) \approx (2\Delta\eta)^{-1} (2\Delta\xi)^{-1} \sum_{\pm} \exp\left[-\frac{(\eta - \bar{\eta})^2}{(\Delta\eta)^2} - \frac{(\xi \mp \bar{\xi})^2}{(\Delta\xi)^2}\right],$$

$$0 \leqslant \bar{\xi} < 1, \quad \text{for} \quad \eta > 0 \quad \text{and} \quad \bar{\xi}^2 \ll 1 \tag{3.8}$$

or for $|\eta| \ll 1$ and $\xi \approx \xi$

$$F(\eta, \xi) \approx e^{-1} F_0 \exp\frac{\eta}{\eta_c} \quad \text{for} \quad 0 < F_0 \equiv F(\eta_c, \xi_c) \ll 1, \tag{3.9}$$

we obtain the estimate, $\eta_c \sim 0.1 \sim (\Delta\eta)^2$ and $\xi_c^2 \sim (\Delta\xi)^2 \sim 0.1$ for typical values $c_a \sim 0.1$ and $c_a^{(2)} \sim 10^{-5} \gtrsim c_{TLS}$ [see (2.4)] in glasses and, apparently, the order of magnitude estimate $F_0 \sim 10^{-2}$. Thus in the cluster model of a glass[7] (Sec. 1)

$$c_a(d) \sim \left(\frac{a_1}{a_2}\right)^d, \quad c_a^{(2)}(d) \sim \left(\frac{a_1}{a_3}\right)^d, \quad d = 3 \ (\text{or} \ d = 2); \tag{3.10}$$

$$c_a \equiv c_a(3) \approx 10^{-1} - 10^{-2} \quad \text{for} \quad a_1 \approx 3\text{Å}, \quad a_2 \approx 6 - 12\text{Å}, \tag{3.11}$$

i.e., $c_a \sim 0.1$ for $a_2 \sim 10$ Å, $c_a^{(2)} \equiv c_a^{(2)}(3) \approx 10^{-5}$–$10^{-6}$ for $a_3 \approx 50$–100 Å, if it is assumed that soft configurations are characteristic for atoms on the "surfaces" of arbitrary clusters, while CTW correspond only to atoms binding "the surface" of clusters of a large a_3.[8,47]

In conclusion, we note the following. For glasses it may

be assumed that typically the function $F(\eta,\xi)$ decreases monotonically or slightly nonmonotonically (for $F_m \lesssim F_0$; Fig. 2) for $\eta < \bar{\eta}$, at the same time, multiwell local atomic potentials with a concentration c_{mw} ($\ll 1$), in particular, two-well potentials ($c^{(2)} \ll 1$), practically reduce to critical two-well potentials, $c_{mw} \approx c^{(2)} \approx c_a^{(2)}$. The concentrations c_a and $c_a^{(2)}$ must decrease from their highest values in glasses to low values in amorphous silicon (a-Si), like the parameters η_c and ξ_c of the function $F(\eta,\xi)$. This is associated with the increase in the mean coordination number from $\bar{z} \approx 2$–2.5 in covalent glasses to $\bar{z} \approx 4$ in a-Si. These concentrations in glass, like η_c and ξ_c also, must decrease as the average density $\bar{\rho}_a$ increases from $\bar{\rho}_a \approx \bar{\rho}_g$ ($c_a \sim 10^{-1}$, $c_a^{(2)} \approx 10^{-5}$–$10^{-6}$) to $\bar{\rho}_a \approx \bar{\rho}_0$($c_a \ll 10^{-1}$–$10^{-2}$, $c_a^{(2)} \ll 10^{-6}$), in particular, as the pressure (p) rises or with annealing (see Refs. 8, 49, and 126). The opposite effect of an increase in c_a, $c_a^{(2)}$, etc. as $\bar{\rho}_a$ decreases was observed in an α-Si film in Ref. 48. On the basis of the general model of soft configurations it is also possible to take into account empirically the observed intermediate order (over distances $\sim a_2$ or $\sim a_3$).

3.2. Low-energy excitations. Density of states. Heat capacity

In soft atomic configurations there arise nonphonon branches of low-energy elementary excitations $\mathscr{E} \ll \hbar\omega_D$, determining the universal properties of glasses at quite low temperatures $T \ll \hbar\omega_D$. These excitations correspond to low-energy excited states (ψ_n, E_n) of quantum, one-mode anharmonic oscillators with the atomic potential (3.1), which for typical values of $c_a \sim 0.1$ may be assumed not to interact with one another in the zeroth-order approximation (see below and Ref. 8). The Hamiltonian of such an oscillator has the form[8,40,52,56]

$$\hat{H} = -\varepsilon_0 \frac{d^2}{dx^2} + V(x) \equiv wh,$$

$$\hat{H}\psi_n = E_n\psi_n \quad (n = 0,\ 1,\ 2,\ \ldots), \tag{3.12}$$

$$\hat{h} = -\frac{d}{dX^2} + K_1X^2 + K_2X^3 + X^4,$$

$$\mathscr{E} = \mathscr{E}_n(\eta,\ \xi) = w\varepsilon_n(K_1,\ K_2) = E_n - E_0, \tag{3.13}$$

$$K_1 \equiv \eta\eta_L^{-1}, \quad K_2 \equiv \xi\eta_L^{-1/2}, \quad X \equiv x\eta_L^{-1/2},$$

$$\varepsilon_0 \equiv \frac{\hbar^2}{2Ma_0^2} \ll w \equiv A\eta_L^2 \approx \hbar\omega_D\eta_L^{1/2} \ll \hbar\omega_D$$

$$\text{for} \quad \eta_L \equiv \left(\frac{\varepsilon_0}{A}\right)^{1/3} \ll 1.$$

Even though there is no general analytic solution to the problem of the spectrum of an anharmonic oscillator in the entire (η,ξ) plane it is still possible to obtain a significant part of the information required below, about the behavior of low levels $E_n(\eta,\xi)$ and excitations with energy $\mathscr{E}_n(\eta,\xi)$ in significant regions $|\eta| \ll 1$ and $\xi^2 \ll 1$. Thus in the case of a symmetric potential for $0 < \eta \ll 1$ and $\xi = 0$ it is possible to construct general formulas determining $E_n(\eta) \equiv E_n(\eta,\xi = 0)$.[50] In this case

$$E_n(\eta = 0) = 3\cdot 2^{-4/3}w\left(n + \frac{1}{2}\right)^{4/3},$$

so that the gap widths $E_{n+1} - E_n$ for $n \geqslant 1$ are much greater than the smallest gap width $E_1(0) - E_0(0) = 1.5w$ for a completely anharmonic oscillator, while

$$E_n(\eta) \approx \hbar\omega(\eta)\left(n + \frac{1}{2}\right)$$

for an almost harmonic oscillator with $\omega(\eta) = \omega_D\eta^{1/2} \ll \omega_D$ for $\eta_L \ll \eta \ll 1$. One can see already from the foregoing that the atomic dynamics in soft configurations is characterized by a new vibrational energy scale $w \ll \hbar\omega_D$ and a corresponding scale η_L for η and ξ^2; namely, here w is the analog of $\hbar\omega_0$ in the tunneling model [in which, however, $\hbar\omega_0 \approx \hbar\omega_D$; see (2.3)]. In reality $w \sim 30$ K and $\eta_L \sim 10^{-2}$ for typical values $\varepsilon_0 \sim 1$ K and $A \sim 30$ eV. The spectrum of energies $\mathscr{E}$ of excitations of the system of oscillators (3.12) is practically continuous in accordance with the continuous nature of the distribution $F(\eta,\xi)$ and the overlapping of the energy bands $\mathscr{E}_n(\eta,\xi)$ for $n \geqslant 1$. In this spectrum there are three basic regions[8]:

$$\mathscr{E} \ll w, \quad \mathscr{E} \sim w \ \text{and}\ w \ll \mathscr{E} \ll \hbar\omega_D, \tag{3.14}$$

corresponding to three classes of excitations of different physical nature (and enumerated by the number $q = 1$, 2, and 3).

Excitations with very low energy $\mathscr{E} = \mathscr{E}_1 \ll w$, corresponding to the lowest excited state E_1, are not vibrational for $E_1(0) - E_0(0) > w$, but arise only because of the small splitting of the ground state $E_0(i)$ in CTW wells ($i = 1,2$) owing to the weak atomic tunneling with amplitude J and/or asymmetry of the potential $2\Delta \equiv |E_0(1) - E_0(2)|$, as soon as the usual condition for the existence of a bound state in each well $\mathscr{E}_1 < V_B$ (V_B is the height of the interwell barrier) holds.[8,40] Such excitations are analogous to TLS, introduced in the tunneling model (Sec. 2b), differing from the latter in a number of respects.[8] Thus unlike the tunneling model in the two types of CTW described above (3.4, 5) there arise two branches of TLS ($j = 1,2$), which, generally speaking, have different properties (see below). The energy of the tunneling TLS of the jth branch [compare (2.4)][8,40] equals

$$\begin{gathered}\mathscr{E}_{TLS}^{(j)} \equiv \mathscr{E}_{q=1}^{(j)} \equiv w\varepsilon_{TLS}^{(j)}(K_1,\ K_2) = 2(J_j^2 + \Delta_j^2) \ll w, \\ J_j \sim \hbar\omega_0^{(j)}\exp(-\lambda_j) \ll w, \quad 2\Delta_j = w|\tau_j|f_j(\zeta_j) \ll w\end{gathered} \tag{3.15}$$

for significant values $|\tau_j| \ll 1$ and barrier height

$$\lambda_j = \gamma_j(2MV_B^{(j)}l_j^2\hbar^{-2})^{1/2} \sim (\zeta_j)^{1/\nu_j} > (\bar{\zeta}_j)^{1/\nu_j}, \quad \gamma_j \sim 1$$

and $1/2 \leqslant \nu_j \leqslant 2/3$ for which the condition $\mathscr{E}_{TLS} < V_B$ holds; at the same time each potential well has an almost harmonic form and $\omega_0^{(j)} \sim w\zeta_j^{1/2}\hbar^{-1}$ is the frequency of almost harmonic oscillations in such CTW, $w < \hbar\omega_0^{(j)} \ll \hbar\omega_D$. Here $\zeta_1 \equiv |K_1|$, $\zeta_2 \equiv 9K_2^2/32 \equiv \tau_1^2$, $\tau_2 \equiv 8(4K_1K_2^{-2} - 1)/9$ and $\zeta_j \approx 10 - 3$; $f_1(\zeta) \sim \zeta^{3/2}$, $f_2(\zeta) \sim \zeta^2$, $\nu_j \approx 2/3$ for $\lambda_j \gg 1$ (the interwell distance $l_j \sim a_0(\eta_L\zeta_j)^{j/2} \gtrsim \alpha_0\eta_L$). Here, unlike (2.3), there is a correlation between Δ_j and λ_j, which can be explicitly manifested in some effects (see Refs. 8 and 51).

Excitations with moderately low energy $\mathscr{E} \sim w$ ($q = 2$), determined in practice by the oscillator equations for E_n for $n = 1$ and in part for $n = 2$, correspond to quasilocal anharmonic oscillations of the atoms, primarily in the singular and partly in the one-well, critical potentials [see (3.3)–(3.5)].[8,52,56] It turns out that for these vibrational excitations the energy $\varepsilon_n(K_1,K_2) = \mathscr{E}_n w^{-1}$ varies nonmonotonically on the K_2 axis as the asymmetry $|K_2|$ increases, and has at least one minimum at the points $K \equiv \{K_1,K_2\} = K_c^{\pm} \equiv \{0, \pm K^*\}$ for $K^* \sim 1$. Moreover, these points are

analytical critical points of the spectrum (see Ref. 53), and in addition both points are equivalent in the sense that $\varepsilon_n(0,K^*) = \varepsilon_n(0,-K^*)$ for $\varepsilon_n(K_1,K_2) = \varepsilon_n(K_1,-K_2)$:

$$\left.\frac{\partial\varepsilon_n(K_1,K_2)}{\partial K_i}\right|_{K_c^\pm} = 0 \quad (i=1,2). \tag{3.16}$$

Taking into account the numerical calculations and topological theorems, about the critical points of the spectrum in the (K_1,K_2) plane,[53,54] it may be concluded that the critical points $K_c^\pm$ are saddle points and at these points the energy of the anharmonic vibrational excitations is $\mathscr{E} \equiv w\varepsilon \sim w$. In Ref. 52 this follows directly from an analysis of the formula

$$\Delta\varepsilon_n = \varkappa_n\left(K_1 - \frac{3}{8}K_2^2\right) \quad (\varkappa_1 = 0.4) \tag{3.17}$$

for $\Delta\varepsilon_n \equiv \varepsilon_n(K_1,K_2) - \varepsilon_n^0$ (with $\mathscr{E}_n \equiv w\varepsilon_n$ and $\varepsilon_n^0 \equiv \varepsilon_n(0,0)$; $\varepsilon_1^0 = 1.5$), obtained from the relations in Ref. 55 with $|K_1| \ll 1$ and $K_2^2 \ll 1$, and from the two facts noted above: the decrease in the contribution of the anharmonicity as $|K_1|$ and/or K_2^2 increase and the translational invariance of the characteristics of multiwell potentials. The conclusion that the critical points $K_c^\pm$ have a saddle character [like the conclusion regarding the function $\varepsilon_1(K_1,K_2)$ for $|K_1| \ll 1$ and $K_2^2 \ll 1$] was drawn in Ref. 56 taking into account the translational invariance, mentioned above, on the basis of the fact that in a numerical calculation of $\varepsilon_1(K_1,K_2)$ it is impossible to construct a topologically consistent picture of isoenergetic lines, if the critical point is a minimum.

Generally speaking, the critical points of the spectrum for $\mathscr{E} \sim w$ do not necessarily reduce to saddle points (a detailed analysis of this question has not yet been performed; there apparently exist preliminary arguments favoring the existence of a minimum also—a critical point for $\varepsilon_n(K_1,K_2)$ for $n \geqslant 2$).

Finally, at higher energies $w \ll \mathscr{E} \ll \hbar\omega_D$ there exist two branches of quasilocal, almost harmonic vibrational excitations ($q=3$), corresponding to both $\mathscr{E}_1$ and/or $\mathscr{E}_2$ for $|K_1| \gg 1$ or $K_2^2 \gg 1$ and generally higher levels, $\mathscr{E}_n$ $(n>2)$.[52,57,58] The spectrum of these excitations, like the spectrum of TLS also (genetically related with it in CTW), does not have critical points. The corresponding vibrational frequencies $\omega_0^{(j)}$ $(j=1,2)$ are related in the usual way with the effective quasielastic constant of the critical potential $k^{(j)}(\eta,\xi)$: $\omega_0^{(j)} \approx (k^{(j)}/M)^{1/2}$ for $k^0 \gg k^{(j)}$ (>0), in particular, $k^{(1)} \sim k^{(0)}\eta$ $(0<\eta \ll 1)$ or $k^{(2)} \sim k^{(0)}\xi^2 \ll k^{(0)}$ (see Sec. 3a). Such excitations make a contribution of the same character as phonons (for $F_0^* \equiv F(0,\bar{\xi}) \neq 0$; see Fig. 2) to the vibrational excitations of the glass.

With regard to the foregoing we shall make the following remarks. It is actually assumed that the elastic and other interactions between oscillators (3.11) and their excitations (3.13), as well as interactions between the latter and excitations of other types (phonons, etc.), do not alter the classification and quasistationary nature of these excitations or the basic results of the theory (though they can give rise to some additional effects—for example, transverse relaxation in a system of many TLS; see Secs. 2b and 3d). A detailed study of this problem has yet to be performed, although for TLS the foregoing has apparently already been largely confirmed within the framework of the tunneling model. Furthermore, the low-energy excitations (3.14) in soft configurations, primarily vibrational, are quasilocal in the same sense as in crystals[17]: their lifetime is finite already as a result of interactions with acoustic phonons, whose spectrum overlaps the spectrum of the excitations (3.14). Finally, as already pointed out, all excitations (3.14) have here the same origin, and are determined by the low excitations of the states of the oscillators (3.11), so that the transition from one class ($q=1,2,3$) to another, accompanied by a change in η and ξ, is continuous, while the density of states of their spectrum $n(\xi)$, determined by the formula (3.2) [for $Q=\mathscr{E}$ and $Q(\eta,\xi) = \mathscr{E}(\eta,\xi)$] can be described by the same expression. However, keeping in mind the different dynamic character of the excitations of these three classes, it is convenient to approximate for $\mathscr{E} \ll \hbar\omega_D$ the expression for $n(\mathscr{E})$ in the form of a sum of the corresponding contributions:

$$\begin{aligned} n(\mathscr{E}) \approx\ & n_{\mathrm{TLS}}(\mathscr{E})\,\theta(\mathscr{E}_a - \mathscr{E}) \\ & + n_{\mathrm{AHV}}(\mathscr{E})\,\theta(\mathscr{E} - \mathscr{E}_a)\,\theta(\mathscr{E}_b - \mathscr{E}) \\ & + n_{\mathrm{HV}}(\mathscr{E})\,\theta(\mathscr{E} - \mathscr{E}_b), \end{aligned} \tag{3.18}$$

where the effective limiting energies $\mathscr{E}_{a,b} \equiv q_{a,b}w$ for $q_a \approx 0.1$–0.3, $q_b \approx 3$, while $\theta(x) \equiv \{1 \text{ if } x>0;\ 0 \text{ if } x<0\}$.

For excitations with the lowest energy, i.e., two branches of tunneling TLS ($j=1,2$), just as in the tunneling model, the density of states depends on the duration of the experiment t_e, while the distribution over Δ and λ, $P(\Delta,\lambda)$, is independent of t_e. It turns out that

$$n_{\mathrm{TLS}}(\mathscr{E},\ t_e) = n_\infty \varphi(\mathscr{E},\ t_e)$$

$$\text{for} \quad \mathscr{E}_{\min} = 2J(\lambda_{\min}) \lesssim \mathscr{E} \ll w, \tag{3.19}$$

$$n_\infty = \lim_{t_e\to\infty} n_{\mathrm{TLS}}(\bar{\mathscr{E}},\ t_e) \quad \text{for} \quad w \gg \bar{\mathscr{E}} > \mathscr{E}_{\min}. \tag{3.20}$$

At the same time n_{TLS} is virtually independent of $\mathscr{E}$, since the variations in $F(\eta,\xi)$ are small for the variations $\delta\eta \sim \delta(\xi^2) \sim \eta_L \sim 10^{-2} \ll \eta_c \sim 10^{-1}$. The weak function $\varphi(\mathscr{E},t_e)$ increases (or decreases) as $\mathscr{E}$ increases like $\mathscr{E}^\alpha$ for $0<\alpha \ll 1$ (or $|\alpha| = -\alpha \ll 1$). Here $\lambda_{\max}$ corresponds to the top boundary of the range of barrier heights $V_{\max}$ which is assumed to be finite (as in the tunneling model), in agreement with the finite energy of the strongest interatomic bonds; for the empirically typical for some glasses $\mathscr{E}_{\min} \lesssim 10^{-6}$ K (see Refs. 34 and 24), $\lambda_{\max} \approx (2MV_{\max}l)^{1/2}/\hbar$ corresponds to a value of $V_{\max}$ ($\gtrsim 1$ eV) not much greater than T_g. In situations typical for glasses[8,40] in (3.19), at least when $F_0 \sim eF_0^*$ where $F_0^* \equiv F(0,\bar{\xi}) \neq 0$,

$$n_\infty \approx \frac{\eta_L^{3/2} w^{-1} F_0 N_0 \bar{\xi}}{f(\bar{\xi})} \equiv \frac{N_0}{T_0^*} \quad \text{for} \quad N_0 \sim 10^{22}\ \mathrm{cm}^{-3}. \tag{3.21}$$

This agrees with the empirical value (2.4) with $T_0^* \approx 10^2$ eV for the plausible typical value $F_0 \sim (1-3)\cdot 10^{-2}$ [see (3.9)]; this could provide an answer to the question of evaluating c_{TLS} in the problem (1) of the tunneling model (Sec. 2.3).

Unlike (2.3), here $P(\Delta,\lambda)$ is almost uniform over Δ [just as $n_{\mathrm{TLS}}(\xi)$], increasing (or decreasing) slightly like $\Delta^\varkappa$ for $|\varkappa| \ll 1$ as Δ increases, but it is not uniform over λ,

$$P(\Delta,\ \lambda) = \sum_j P^{(j)}(\Delta,\ \lambda),$$

for $0 \leqslant \Delta \ll w$ and $\lambda_{\min} \equiv (\lambda_j(\bar{\xi}_j))_{\min} \leqslant \lambda < \lambda_{\max}$, $\lambda_{\min} \sim 3$; $P(\Delta,\lambda)$ has a maximum at some $\lambda = \lambda_0$, decreasing as $\lambda^{-(3-j)/3}$ for large $\lambda > \lambda_0$, and λ_0 is apparently closer to $\lambda_{\min}$ than to $\lambda_{\max}$.

The dependence of $n_{TLS}(\mathscr{E}, t_e)$ on t_e here differs appreciably from $\ln t_e$ precisely because $P(\Delta,\lambda)$ is not uniform as a function of λ [8,40]:

$$n_{TLS}(\mathscr{E}, t_e) \backsim p(\mathscr{E}, t_e),$$

$$p(\mathscr{E}, t_e) = 1 - \left[1 + L^{-1}(\mathscr{E}) \ln \frac{t_e}{\tau_{min}(\mathscr{E})}\right]^{-1/3}, \qquad (3.21')$$

$$L(x) \equiv 2\ln \frac{w}{x},$$

where

$$\tau_{min}^{(j)}(\mathscr{E}) = \tau(\mathscr{E}, J) \exp[2(\lambda_m^{(j)} - \lambda)], \quad \lambda_m^{(j)} \approx \ln \frac{2\hbar\omega_0^{(j)}}{\mathscr{E}}$$

for $\hbar\omega_0^{(j)}$ from (3.15). As a function of t_e $p(\mathscr{E}, t_e)$ reduces to $\ln t_e$ from the tunneling model only for sufficiently small values of $t_e \lesssim \bar{\tau} = \tau_{min}(\mathscr{E})(w/\mathscr{E})^2$, but the dependence is much weaker for $t_e \gg \bar{\tau}$ (typical values are $\bar{\tau} \sim 10^{-5}$ s for $w \gg \mathscr{E} \approx 0.1 - 1$ K). This fact and the existence of two types of TLS may make it possible to eliminate the inconsistency, pointed out in Ref. 18, between the tunneling model and the experimental data.

The density of states $n_{AHV}(\mathscr{E})$ of quasilocal anharmonic vibrational excitations with energy $\mathscr{E} \sim w$ is determined by the sum of the regular $n_R(\mathscr{E})$ and singular $n_S(\mathscr{E})$ parts. Here $n_R(\mathscr{E})$ is of the same scale as $n_{TLS}(\mathscr{E}, t_e \to \infty)$, extrapolated for $\mathscr{E} \sim w$; in particular, below the first critical point of the spectrum $\mathscr{E}_{c1} \sim w$ for $\mathscr{E} < \mathscr{E}_{c1}$ and $\mathscr{E} \sim w$, it should be expected that (see Refs. 54 and 62)

$$n_R(\mathscr{E}) = p_2 \left(\frac{\mathscr{E}}{\mathscr{E}_{c1}}\right)^2, \quad p_2 \sim F_0 N_0 \eta_L^{3/2} w^{-1}, \qquad (3.22)$$

for $n_R(\mathscr{E}) = n_R(-\mathscr{E})$.[52] The function $n_S(\mathscr{E})$ is determined here by the sum of contributions of the critical points [see (3.16), and also Refs. 54 and 62],

$$n_{AHV}(\mathscr{E}) \approx n_R(\mathscr{E}) + n_S(\mathscr{E}),$$

or, for $|\mathscr{E} - \mathscr{E}_{c1}| \ll w$ and $\delta < w$, $\varepsilon \ll w$,

$$n_{AHV}(\mathscr{E}) \approx n_S(\mathscr{E}) \sim F_0 \eta_L^{3/2} w^{-1} N_0 \ln \frac{w}{|\mathscr{E} - \mathscr{E}_c| + \delta}, \qquad (3.23)$$

when $F_0 \sim F_0^* \neq 0$. The width of this entire band of the spectrum is of the order of w, though it is somewhat smaller; the height of the peak is $n_S(\mathscr{E}_{1c}) \gg n_R(\mathscr{E}_{1c})$, i.e., it stands out appreciably against the regular phonons (see Ref. 8, p. 284). Since for anharmonic oscillations $\mathscr{E}_1$ is appreciably smaller than even $\mathscr{E}_2 - \mathscr{E}_1$ (see above), the contribution of the oscillator levels E_0 and E_1 is largest in the region $\mathscr{E} \sim w$. In the approximation in which only the contribution of these levels and therefore excitations with energy $\mathscr{E} = \mathscr{E}_1 \lesssim w$ is taken into account, the latter can be interpreted as effective TLS. For such vibrational TLS, however, $n_{AHV}(\mathscr{E})$ does not depend on t_e (for real $t_e \gg \hbar/w \sim 10^{-12}$ s), unlike $n_{TLS}(\mathscr{E}, t_e)$ for tunneling TLS. In agreement with (3.9), a rough estimate of the concentration c_{AHV} of centers of such vibrations gives $c_a \sim 0.1 > c_{AHV} \sim c_a^{(3)} \approx 10^{-2}$–$10^{-3}$ ($\gg c_{TLS}$).

Finally, for quasilocal harmonic vibrational excitations, realized in the same two-well potentials as the tunneling TLS and in a significant fraction of the single-well potentials, the density of states has a Debye form, at least when $F_0 \sim F_0^* \neq 0$ (see, however, Refs. 57, 58, 124):

$$n_{HV}(\mathscr{E}) = N_0 D_0 F_0^* \omega^2 \quad \text{for} \quad \hbar\omega_D \gg \mathscr{E} \equiv \hbar\omega \gg w,$$

$$D_0 = \gamma_0 \eta_L^{3/2} \left(\frac{\hbar}{w}\right)^3 \sim \gamma_0 \omega_D^{-3}, \quad \gamma_0 \sim 1, \quad n_{HV}(w) \sim n_R(w). \qquad (3.24)$$

The heat capacity of glass $C_g(T)$ at sufficiently low temperatures $T \ll \hbar\omega_D$, determined by the excitations under study, is expressed, as usual, in terms of their density of states. For very low temperatures $T \ll w$ the heat capacity is determined by the contribution of tunneling TLS, and the expression for $C_g(T)$ has the form [see (3.19)–(3.21)]

$$C_g(T) \approx C_{TLS}(T) \approx \beta_g T^{1+\alpha}, \quad |\alpha| \ll 1,$$

$$\beta_g \equiv \beta_g(t_e) \sim n_\infty. \qquad (3.25)$$

This relation can be made to agree with the empirical formula (2.1) for $0 < \alpha = n \ll 1$ [see the discussion in connection with (3.21) for the dependence on t_e].

At moderately low temperatures $T \sim w$ $C_g(T)$ is determined here by the anharmonic vibrations (3.23), and the sum of Schottky contributions $\propto (\mathscr{E}/2T)^2 \operatorname{ch}^{-2}(\mathscr{E}/2T)$ for the effective vibrational "TLS" in the region of the peak in the density of states $n_{AHV}(\mathscr{E})$. At the same time $C_g(T)/T^3 \approx C_{AHV}(T)/T^3$ has a t_e-independent maximum of width $\lesssim w$ in the region $T \sim w$,[52] which agrees qualitatively with the observed "hump" $\alpha_g(T_m)$ for $\alpha_g(T)$ in (2.1) for $5 \lesssim T \lesssim 30$ K and $T_m \approx 15$–30 K (see Fig. 1).

Finally, at higher temperatures $T \gg w$ the contribution of the harmonic vibrations (3.24) to $C_g(T)$ has a Debye form[57,58]:

$$C_{HV}(T) \approx \frac{4\pi^4}{15} N_0 F_0^* D_0 T^3. \qquad (3.26)$$

It remains unclear, however, whether or not this contribution is significant for the empirical excess Debye heat capacity ($\alpha_g^0 T^3$) in (2.1). For this part of the heat capacity the simultaneous contribution of "soft" acoustic modes [with $(\omega_l)_{max} \ll \omega_D$, if such modes exist in glasses] and vibrational excitations, whose density of states is characterized by a peak at $\mathscr{E} \sim 30$ K, of the type (3.23) (see Refs. 59–61), may turn out to be significant.

3.3. Scattering effects. Heat conduction

In the theory under study resonance and relaxation scattering processes and the absorption of acoustic (phonons) and electromagnetic (photons) waves, as well as scattering of neutrons, described by quasilocal nonphonon excitations (3.14), should determine most of the universal unusual properties of glasses at quite low temperatures T or for quite low energies $\hbar\omega$ (transfer of energy ΔE) of the scattered "particles," at least for $T \lesssim w \approx 10$–30 K or $\hbar\omega \lesssim w$, $\Delta E \lesssim w$ (in the tunneling model only the TLS play the role of such excitations). As usual, the interaction of low-energy excitations of the glass with an electromagnetic wave gives rise to appreciable scattering (absorption) effects, when for these excitations the characteristic magnitude of the electric dipole, for the diagonal or off-diagonal matrix element, is high enough, $p_0 \approx 10^{-18}$–10^{-17} CGSE. Such values of p_0 are realistic in a number of nonmetallic glasses (a-SiO_2, a-As_2S_3, etc.), being determined by the asymmetry of the local chemical bonds in soft atomic configurations (some particular realizations of this asymmetry are discussed, for example, in Ref. 93).

The interaction of TLS ($q = 1$) *and, apparently, also of* quasilocal excitations (3.23) ($q = 2$) with low-frequency phonons is determined by a mechanism similar to the "strain potential" and arises because of the change in the form of the

critical potential (3.1) in the field of the wave[8,63–65] (compare the mechanism of Ref. 66). The external, relative to the oscillators (3.12), "field" Λ should change the configurational parameters (η,ξ) and the spectrum of these excitations:

$$\eta \to \tilde{\eta}_{qj}(\Lambda) = \eta + \delta\eta_{qj}(\eta,\ \xi;\ \Lambda),\quad \mathscr{E}_{qj} \to \tilde{\mathscr{E}}_{qj}(\eta,\ \xi;\ \Lambda),$$
$$n(\mathscr{E}) \to \tilde{n}(\mathscr{E};\ \Lambda)\quad \text{etc.},\quad q = 1,\ 2,\quad j = 1,\ 2. \tag{3.27}$$

Here Λ can be the parameters of the acoustic (e_0) or electromagnetic wave as well as the variations of the parameters of the system (the density ρ_a, the conduction electron density, or the quantum numbers of the electronic state). The Hamiltonian describing the coupling of the excitations with low-frequency phonons $\hat{H}_1$ and the coupling parameter $b_1^{(qj)}(\eta,\xi)$ have the form (see Ref. 64)

$$\hat{H}_1 = V(x;\ \tilde{\eta}_{qj}(e_0),\ \tilde{\xi}_{qj}(e_0)) - V(x;\ \eta,\ \xi) \approx e_0 f_{qj}(x),$$
$$|e_0| \ll 1, \tag{3.28}$$
$$b_1^{(qj)}(\eta,\ \xi) = \varkappa_{qj}^{(1)}(\eta,\ \xi)\frac{\partial\mathscr{E}_{qj}}{\partial\eta} + \varkappa_{qj}^{(2)}(\eta,\ \xi)\frac{\partial\mathscr{E}_{qj}}{\partial\xi},$$
$$b_1^{(1j)}(\eta,\ \xi) = b_\Delta^{(j)}(\eta,\ \xi)\frac{\partial\mathscr{E}_{1j}}{\partial\Delta} + b_J^{(j)}(\eta,\ \xi)\frac{\partial\mathscr{E}_{1j}}{\partial J}, \tag{3.29}$$

where

$$f_{qj}(x) = \varkappa_{qj}^{(1)}x^2 + \varkappa_{qj}^{(2)}x^3,\quad \varkappa_{qj}^{(1)} = \frac{\partial\tilde{\eta}_{qj}}{\partial e_0},$$
$$\varkappa_{qj}^{(2)} = \frac{\partial\tilde{\xi}_{qj}}{\partial e_0},\quad \delta\mathscr{E}_{qj} = b_1^{(qj)}e_0.$$

Unlike the tunneling model, here $b_1^{(qj)}$ are random quantities, whose distribution density can be quite broad, and the corresponding mean values $\bar{b}_1^{(qj)}$ can differ appreciably in magnitude and have a different sign even for different branches $(j = 1,2)$ of the same class (q) of excitations, in particular, for both branches of TLS, as proposed on an empirical basis in Ref. 18. For tunneling TLS $|\bar{b}_1|_{\max}$ is much larger than the expected scale $\hbar\omega_D$[8,40]:

$$|\bar{b}_1^{(1j)}|_{\max} \equiv |\bar{b}_{\text{TLS}}^{(j)}|_{\max} \approx \frac{\hbar\omega_D}{\bar{\zeta}\eta_L} \approx 0.3-1\ \text{eV} \tag{3.30}$$

for characteristic $k \approx k^{(0)}\bar{\zeta}\eta_L \ll k^{(0)}$ with $\bar{\zeta} \approx 10$–3 in accordance with (2.10), while for the excitations (3.23) it is more likely that

$$|\bar{b}_1^{(2j)}|_{\max} \equiv |\bar{b}_{\text{AHV}}^{(j)}|_{\max} \sim w\eta_L^{-1} \approx 0.1-0.3\ \text{eV}.$$

Such a large value of $|\bar{b}_1| \gg \hbar\omega_D$ (it is usually of the order of $\hbar\omega_D$) arises as a result of the softness of the configurations $(k \ll k^0)$, whose generalized susceptibility $\varkappa(\approx k^{-1})$ is high. To find $b_1^{(qj)}(\eta,\xi)$ (or $b_{\Delta,J}^{(j)}(\eta,\xi)$ and their probability density function $\rho(b_1^{(qj)})$ it is necessary to take into account the following[8,19,40,67] (see also Refs. 15, 16, 18). The interaction of TLS and the excitations (3.23) with high-frequency $(\omega > \omega_c)$ "phonons," adiabatically following the motion of the "atom" in a separate well of the critical potential (3.1), should lead only to a constant renormalization of the parameters of the potential, which may be regarded as already taken into account. However, real relaxation processes and polaron type restructuring of the excitation as well as their coupling parameters with the medium are determined by the interaction with low-frequency phonons $(\omega < \omega_c)$, in particular, it is precisely the latter that affect in a decisive manner the tunneling of atoms[67] (see also Ref. 19). At the same time here the limiting frequency is $\omega_c = w/\hbar$, $\mathscr{E}_{\text{TLS}} \ll w \ll \hbar\omega_D$.[8] This separation of the contributions for a tunneling atom, interacting with excitations of the electronic fluid of the metal, was first explicitly traced in Ref. 67a. In the situation at hand this separation can apparently also be made in the approach of Ref. 67, and the corresponding calculations for $b_1^{(qj)}(\eta,\xi)$ and $\rho(b_1^{(qj)})$ have yet to be performed. An attempt was recently made to calculate $b_{\text{TLS}}^{(j)}$ by directly averaging the contribution (e_1) of the high-frequency oscillations in the Hamiltonian for the coupling of the TLS with the field of the atomic vibrations $\tilde{e} = e_0 + e_1$ (see Ref. 51).

In the theory under discussion the phonon thermal conductivity χ_g of the glass at very low temperatures $T \ll w \approx 10$–30 K, as assumed also in the tunneling model (see Sec. 2.2), is determined by the resonance scattering of thermal phonons by TLS [on that one of their branches on which the coupling parameter $|\bar{b}_1|$ is largest, see (3.30)]. At the same time, taking into account (3.19) we have $\chi_g \propto T^{2-\alpha}, |\alpha| \ll 1$, and the best agreement with the empirical dependence (2.2) is achieved for $0 < \alpha \ll 1$. At moderately low temperatures $(T \sim w)\chi_g(T)$ can be determined by resonance scattering $(\hbar\omega = \mathscr{E})$ of thermal phonons by vibrational excitations (3.22) and (3.23): the effective phonon mean-free path is $l_{\text{ph}}^*(x,T) \sim [n_R(2xT)2xT\,\text{th}\,x]^{-1}(x \equiv \hbar\omega/2T)$, so that $\chi_g \propto T^3 l_{\text{ph}}^*(1/2,T) \approx \text{const}$, corresponding to the plateau near $T \approx w$ in a region of width $\lesssim w$, in agreement with the empirical dependence $\chi_g(T)$ at temperatures $5\ \text{K} \lesssim T \lesssim 30\ \text{K}$ [see (2.2) and Fig. 1][52] (see Ref. 3 and also Ref. 60 for a discussion of other interpretations of the plateau for $\chi_g(T)$; possible mechanisms for $\chi_g(T)$ at higher temperatures T, $w \ll T \ll \hbar\omega_p$, are discussed in Refs. 3 and 56).

The theory under study predicted in a natural manner[15] that the cross section $\sigma_i(\mathbf{q},\Delta E)$ for inelastic scattering of neutrons, proportional to the density of the scattering excitations $n(\mathscr{E})$[62], $\sigma_i(\mathbf{q},\Delta E) \propto n(\mathscr{E})$ for scattering inelasticity $\Delta E = \mathscr{E}$, should contain a peak at $\Delta E \approx w \approx 10$–30 K. This peak corresponds to the scattering of neutrons by the excitations (3.23), whose density of states has a peak at $\mathscr{E} \approx w$, and its width is comparable to, but less than, w. This peak in the neutron scattering near $\Delta E \approx 20$ K in a-SiO_2 glass was found independently in Ref. 68, where the scattering excitations (3.23) are associated with the coupled rotational motions of SiO_4 tetrahedra. On the basis of the model of soft configurations (3.1) the concentration of anharmonically vibrating atoms, corresponding to the excitations (3.23), was evaluated from empirical data[68]: $c_{\text{AHV}} \sim 0.01$, which is consistent with the estimate made above. It is possible that the low-energy peaks at ≈ 10–30 K in the Raman scattering and IR absorption spectra,[3] observed in a number of glasses (a-SiO_2, and others), are determined by the interaction of the IR radiation with the same excitations (3.23) (compare Ref. 46). The tensor characterizing the intensity of the scattered light with a frequency shift $(-\Delta\omega)$ in an amorphous medium,[3] $\hat{I}^{(R)}(\Delta\omega) \propto n(\mathscr{E} = \hbar\Delta\omega)$, has a peak corresponding to the peak (3.23). It is also possible that the strong scattering of phonons with $\hbar\omega \approx 10$–20 K observed in glasses (a-SiO_2 and others)[69] is determined by their coupling with the excitations (3.23), as soon as the average binding energy $|\bar{b}_{\text{AHV}}|$ c_{AHV} can be comparable to $\hbar\omega \approx w$ [compare $|\bar{b}_{\text{TLS}}|c_{\text{TLS}}(\mathscr{E}_0 = 1\ \text{K}) \ll \mathscr{E}_0$].[97]

3.4. Concluding remarks

The foregoing theory of low-energy excitations in glasses is based on the reduction of the set of structural parameters of the local atomic configurations to only two basic parameters (η,ξ). This theory, in which the behavior of the density of states $n(\mathscr{E})$ agrees reasonably well with experiment and anharmonic vibrations (3.23) are predicted with the universal energy scale $w \approx 10$–30 K and a corresponding peak in the neutron scattering, actually gives the solution to the problems (1)–(4a) and (5) of the tunneling model and apparently the key to the solution of the problem (4b), noted in Sec. 2.3. The tunneling model appears to be a particular case of the model of soft configurations for $\mathscr{E} \lesssim \mathscr{E}_a \ll w$, in which the important problem is the problem of determining the structure of the "atom" in the soft configuration in a specific glass. The excitations of interest are actually quasistationary for $\mathscr{E} \lesssim w$, and the basic parameters of the system w, η_L, and F_0, generally speaking, depend on T_g, for $T_g \propto T_m \propto A$, corresponding to some correlation between the structure of the glass for $T \ll T_g$ and vitrification.[2,3,32] At the same time $n_{TLS}(\mathscr{E},T_g) \propto T_g^{-\gamma} F_0^g(T_g) \propto C_g(T \lesssim 1\ \mathrm{K})$ and $|b_{TLS}| \propto T_g^{\varkappa}$ for $\gamma = 1 = \varkappa$, which agrees with the experimental data[31,32] for $|b_{TLS}|$ and, for a suitable assumed $F_0(T_g)$, for $n_{TLS}(\mathscr{E},T_g)$.

Among the problems of the theory we call attention first to the analysis of the explicit form of $F(\eta,\xi;T_g)$ in specific models of the glass structure, which is equivalent to determining the explicit structure of the "atom" in the soft configuration, and the interactions of excitations with phonons and with one another (compare also Refs. 20, 70, 71, and 76).

4. ANOMALOUS ELECTRONIC PHENOMENA IN NONMETALLIC GLASSES

4.1. Some basic empirical facts

The anomalous character of many electronic properties of nonmetallic glasses is ultimately determined by the presence of specific electronic localized states, as a rule absent in crystals, in the mobility gap of width $E_g = E_v^* - E_c^*$, i.e., in the region of localized states, separated by mobility thresholds E_v^* and E_c^* from regions of nonlocalized states—valence (v) and conduction (c) "bands" (see Ref. 74). States of impurity centers or local structural defects (see Refs. 7, 72, and 73) play an important role in dielectric glasses, while in glassy semiconductors the states of the characteristic local centers are of primary importance. For glassy semiconductors (chalcogenide glasses, etc.) two sets of electronic properties have been discovered which are incompatible in the traditional one-electron theory and which depend weakly on the concentration c_i ($\ll 1$) of impurity atoms injected during the preparation of the glass.[2,74] Thus the energy W_a of activation of the electrical conductivity $\sigma = \sigma_0 \exp(-W_a/T)$, i.e., the position of the Fermi level ζ in the gap depends weakly on c_i, T, and the electric field F for $10^{-6} \lesssim c_i \lesssim 10^{-2}$–$10^{-1}$, $T \lesssim T_g/2$ and $F \lesssim 10^6$ V/cm, as does the energy of the main peak of the photoluminescence E_{PL}, and this indicates that the density of states $g(\bar{E})$ at the center of the gap is high. On the other hand, in thermal equilibrium there is no paramagnetism, which appears under illumination (photo-EPR), and the intrinsic optical absorption edge (minus the weak Urbach tail) is sharp (and there is no Mott conductivity at the Fermi level[74–76]), i.e., as if $g(\bar{E}) \approx 0$. The following relations were found empirically for glassy semiconductors:

$$E_{opt} \approx 2E_{PL} \approx 2E_{IA} \approx E_X(\mathrm{PL}) \approx 2W_a \approx E_{PC} \approx E_g, \quad (4.1)$$

$$I_{PL} = I_0 \exp\left(-\frac{T}{T_A}\right)$$

$$\text{for } T'_A \lesssim T \leqslant \frac{1}{2}\hbar\omega_D/2 \text{ and } T'_A \approx T_A \approx 20\text{–}40\ \mathrm{K}, \quad (4.2)$$

where E_{PC}, E_{IA}, and $E_X(\mathrm{PL})$ are the thresholds for photoconductivity, intragap absorption, and excitation of photoluminescence, whose fading (suppression with time under illumination), unlike its intensity I_{PL}, depends slightly on T.

4.2. Anderson's phenomenological model

The following hypothesis was proposed in order to eliminate the obvious inconsistency noted above[2,77]: the stationary states in the gap are populated only by single (with spin $\sigma = 0$) electron pairs with a negative correlation energy $U = E(2) + E(0) - 2E(1) < 0$ ($E(n)$ is the energy of the state occupied by n electrons; $n = 0, 1, 2$). The interelectronic attraction, as also in the case of polarons (see Refs. 76–79), appears here in the intrinsic structure of the glass owing to the deformation of the medium and the corresponding gain in energy $\delta E < 0$, $U = U_c + \delta E < 0$ with an interelectronic repulsion energy $U_c < |\delta E|$. This phenomenological model of the states in the gap is described by the Hamiltonian[2,77]

$$\hat{H} = \hat{H}_e + \hat{H}_{ee}, \quad \hat{H}_e = \sum_{i,s} E_i \hat{n}_{i,s}, \quad \hat{H}_{ee} = \sum_i U_i \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}, \quad (4.3)$$

where $\hat{H}_{ee}$ is the Hubbard interaction operator (see Ref. 80), a particular case of the Shubin-Vonsovskiĭ polaron model,[81] for the case of attraction with $U_i < 0$; $\hat{n}_{is}$ is the occupation number operator; and, $s = \pm(1/2) \equiv (\uparrow,\downarrow)$. Here it was assumed that the one-electron terms E_i at the sites (i) correspond to a wide probability density distribution $\rho(E_i)$ in the gap, and in addition $\rho(E_i) \gtrsim 10^{19}$–$10^{20}$ cm^{-3} eV^{-1}, while the energies U_i correspond to a narrow probability density distribution $f(U_i) \approx \delta(U - U_i)$ with very large $|U| = -U \sim 1$ eV; the latter can hardly be determined by the usual polaron effect (see Refs. 77–79, 82 and Sec. 5 below). As a consequence the density of states $g(E)$ is generally large in the gap, and even $g(\bar{E}) \gtrsim 10^{19}$–$10^{20}$/cm^3 eV. In this model there arose the problem, among others mentioned below, of the nature of the empirically determined local charged centers and almost discrete energy levels [$\approx E_g/4$, $\approx E_g/2$; see (4.1) and Ref. 74] in the gap (see also Refs. 83–85).

4.3. Model of "coordination defects"

This problem is solved in an alternative model,[86,87] which is also based on Anderson's hypothesis,[7] by means of the following assumption. The states in the gap belong to specific "coordination defects" in the structure—atoms whose coordination number z does not equal the normal number z_0, $z = z_0 \pm 1$. The transformation of two neutral defects D^0 (with spin $\sigma = \pm 1/2$) into a pair of charged (with spin $\sigma = 0$) defects is similar to the exothermal reaction

$$D^0 + D^0 \rightarrow D^+_{z_0+1} + D^-_{z_0-1}, \quad (4.4)$$

in which the energy released plays the role of the correlation

energy $U(<0)$ of a pair of independent defects (a pair with an alternative valence). At the same time the scheme of the energy levels of such defects in the gap is constructed taking into account the existence of empirically established, almost discrete levels ($\approx E_g/4$, $\approx E_g/2$ for $|U|\approx E_g/2\sim 1$ eV against the background of an otherwise practically empty gap. Unlike the model (4.3) this model is based on taking into account the specific chemical properties of the atoms of the material, primarily the atoms of the chalcogen (S, Se, Te; $z_0=2$), containing "unshared pairs" of electrons participating weakly in the formation of the covalent bonds (singlet), rather than the characteristic features of the amorphous structure of the glass.

* *

Both models lead to a number of important consequences, including the predominance of diamagnetism and the weak effect of external factors (c_i,F), which are in accord with the experimental data; the ground and metastable excited states of electron pairs must play the role of centers of the effects characterized by the relations (4.1) (see Refs. 74, 77, 2, 83, 88, 90–99). At the same time there arose in these models and in the comparison of these models with experiment a number of serious problems (see also Refs. 88, 89, 100–103, 105), concerning the general nature of electron pairs with $U<0$ and such large values $|U|\sim 1$ eV, of $g(\bar{E})$ ($g(\bar{E})\approx 10^{19}$–$10^{20}/\text{cm}^{-3}\,\text{eV}^{-1}$ or $g(\bar{E})\approx 0$), the nature of the quasidiscrete terms ($\approx E_g/4$, $\approx E_g/2$), and the binding $|U|\approx E_g/2$ in the gap, as well as the relations between the centers of different processes in a glassy semiconductor and, finally, the connection between the electron pairs and the characteristics of the structure of the glass, determining its low-temperature properties. This could indicate that the structure of the states in the gap is more complicated than assumed in the models (4.3) and (4.4). The question of the uniqueness of the concept of a point defect in the glass, employed in the model (4.4), is also a difficult one (see below and Ref. 34).

5. LOCALIZED ELECTRONIC STATES IN GLASSES

A more general approach, which makes it possible to construct an essentially microscopic theory of localized electronic states in the *intrinsic structure* of the glass and of the phenomena determined by them in glassy semiconductors as well as to solve the problems of the models (4.3) and (4.4), is based on the idea of self-trapping of electrons in soft atomic configurations of the glass.[8,39,104]

5.1. Self-trapped states. Electron pairs with negative correlation energy

Usually, in particular for polarons,[79] the interaction of an electron with its nearest neighbor atoms, which determines the self-trapping of the electron, is strong and has a characteristic energy (the constant in the strain potential, etc.) of the order of several electron volts, but is rarely realized because of the large elasticity ($k\approx k^{(0)}\equiv M\omega_D^2$), hindering the deformation of the medium (see Sec. 3.1) or the significant average velocity of an untrapped electron. At the same time the self-trapping (ST) energy is $W_1<0$, i.e., the gain in the energy of the system owing to the interaction of the electron with the medium it deforms and the characteristic atomic displacement $u_p\equiv a_0x_p$ are small: $|W_1|\ll\hbar^2/2m_ea_1^2\sim 1$ eV and $u_p\ll a_0\approx 1$ Å. The self-trapped (ST) electronic states of interest here differ strongly in this and other respects from polaron states. Specifically these ST states are formed primarily owing to the interaction of an electron with a "bare" (in an undeformed medium) localized state ψ_q of a small size $\rho_q\approx a_1$, with an energy level E_q in the tail of the corresponding band, with a weakly coupled "atom" in the soft configuration (3.1) in the region of localization of ψ_q.[104] For a random parameter $Q_q(>0)$ of this interaction the distribution may be assumed to be narrow: $Q_q\approx Q_q(a_1)\approx Q_0\gg Q_q(\rho_q)$ for $\rho_q\gg a_1$ with the typical value $Q_0\approx 3$ eV. At the same time a strong electron-atom interaction is realized largely (if not completely) precisely because $\rho_q\approx a_1$ and the soft configuration is comparatively easily restructured owing to the smallness of the quasielastic constant of the "atom" $k\ll k^{(0)}$ (3.3)–(3.5). When an electron occupies the state ψ_q (with spin ↑, for example) the "atom" in the field of the electron experiences a significant displacement $|x|$, comparable to unity (at the same time the surrounding medium is strongly deformed), while the magnitude of the drop in the electronic level $J_q(x)\equiv E_q(x)-E_q(<0)$ is comparable to Q_0, while the increase in the potential energy of the "atom" is comparatively small and also comparable to Q_0, $V(x)\lesssim 0.1A\sim Q_0$ for $k\lesssim 0.1\ \text{K}^{(0)}$. Ultimately the energy of the system as a whole drops strongly, i.e., by an amount comparable to Q_0, and a ST state of the electron is formed with a considerable $|W_1|\lesssim Q_0$ and an equilibrium displacement of the "atom" $|x_1|\lesssim 1$. The addition of a second electron with opposite spin (↓) increases the equilibrium displacement of the "atom," $|x_2|>|x_1|$, and the ST energy. For a singlet ($\sigma=0$) electron pair $|W_2|>|W_1|$ (the foregoing discussion concerning the electron states is true, with a trivial modification, for hole states also). At the same time the highest values possible for stable pair states (see below) $|x_2|_{\max}$ and $|W_2|_{\max}$ are extremely large, $|x_2|_{\max}\sim 1$ and $|W_2|_{\max}\sim Q_0$, unlike the values for polaron and other ST states. The energy of the ST states here is described by the expressions[8,79,104]

$$E(n)\equiv E_n(x_n)=nE_q+W_n+U_c\delta_{n,2}+\text{const}\qquad(n=1,\ 2),\tag{5.1}$$

$$W_n\equiv W_n(x_n)<0,\quad W_n(x)=V(x)+nJ_q(x)\text{ and }U_c\equiv U_c(x_2)>0;\tag{5.2}$$

here $\delta_{n,2}\equiv\{1\text{ if }n=2;\ 0\text{ if }n\neq 2\}$, and

$$W_n=\tilde{W}_n^{(H)}(k)\approx-\frac{Q_0^2n^2}{2ka_0^2}<0\qquad\text{for}\quad k^{(0)}\gg k^*=p^*Q_0^{2/3}A^{1/3}a_0^{-2},\tag{5.3}$$

$$\tilde{W}_n^{(AH)}\approx\tilde{W}_n^{(H)}(k^*),\quad|\tilde{W}_2^{(AH)}|\approx\varepsilon_g(Q_0)=2p_1Q_0\left(\frac{Q_0}{A}\right)^{1/3}\qquad\text{for }0\leqslant k\leqslant k^*,\quad 2p_1\sim 1\sim p^*,\tag{5.4}$$

when the equilibrium displacement x_n equals, respectively, almost harmonic ($W_n\sim x_n^2$, $x_n^{(H)}\approx nQ_0/ka_0^2$) or anharmonic ($W_n\propto x_n^4$, $x_n^{(AH)}\approx x_n^{(H)}(k^*)$) values. The ST singlet pair state is stable when its correlation energy is $U=E(2)+E(0)-2E(1)<0$,

$$U=\tilde{U}^{(H)}(k)=U_c-\frac{Q_0^2}{ka_0^2}<0\quad\text{for}\quad k^{(0)}\gg k>k^*,\tag{5.5}$$

$$= \tilde{U}^{(\mathrm{AH})} = \tilde{U}^{(\Gamma)}(k^*)$$
$$= U_c - \frac{1}{2}\varepsilon_g(Q_0) < 0 \quad \text{for } k^* \gtrsim k \geqslant 0, \tag{5.6}$$

for

$$U_c < \frac{1}{2}\varepsilon_g(Q_0),\ k < k_l = \frac{Q_0^2}{U_c a_0^2}\ (< k^{(0)}),\ \ \tilde{U}^{(\mathrm{H})}(k_l) = 0, \tag{5.7}$$

and $Q_0 A^{-1} > \varphi(\eta,\xi)$ [mainly for $\varphi(\eta,\xi) \approx |\eta||\xi|$]. These criteria hold for a significant fraction of the atoms for (3.1), for the typical values $U_c \sim 0.3$ eV and $Q_0 \sim 3$ eV, which corresponds to a significant concentration of such pairs in glassy semiconductors [see (4.14)].[79,82] The relations (5.1)–(5.7) actually correspond to the adiabatic approximation for electrons in the states ψ_q for $\hbar\omega_D \ll Q_0 \ll A$, and here, as in the theory of polarons, $W_2 = 4W_1$ and $|J_q(x_2)|:V(x_2) = 1$. The adiabatic local potential $W_n(x)$ remains critical, since the parameters η and ξ renormalized by the electron-atom coupling remain small in magnitude [see (3.27)][106]:

$$\begin{aligned} \eta \to \eta_n &\equiv \eta(\Lambda) \\ &= (\eta + nq^{(2)})[1 + 3\lambda_n^{-1}(\varkappa_n^2 + 2\varkappa_n)], \quad |\eta_n| \ll 1, \\ \xi \to \xi_n &\equiv \xi(\Lambda) = (\xi + nq^{(3)})(1 + \varkappa_n), \quad \xi_n^2 \ll 1 \end{aligned} \tag{5.8}$$

for $q^{(j)} \equiv A^{-1}(\mathrm{d}^j J_q(x)/\mathrm{d}x)|_{x=0}$ and $|q^{(j)}| \ll 1$; here $\varkappa_n$ is the root of the equation $\varkappa^3 + 3\varkappa^2 + \lambda_n\varkappa + \rho_n = 0$ with $\lambda_n \equiv 8(\eta + nq^{(2)})(\xi + nq^{(3)})^{-2}$ and $\rho_n \equiv 16nq^{(1)}(\xi + nq^{(3)})^{-3}$ which vanishes at $n = 0$.

Since $|W_2(k=0)| = |W_2(k^*)| = \varepsilon_g(Q_0) \sim Q_0$ for $U < 0$, we distinguish two cases:

$$\varepsilon_g(Q_0) \gtrsim E_g \quad \text{or} \quad E_g > \varepsilon_g(Q_0)\ (\gg U_c), \tag{5.9}$$

for glassy semiconductors ($E_g \approx 1$–3 eV) or dielectric glasses ($E_g \approx 5$–10 eV), respectively. In the first case (5.9) the spectra of the quantities $|U|$ and $|W_2|$ have an upper limit, so that

$$\begin{aligned} |W_2| \leqslant |W_2|_{\max} &\equiv W_{\max} = 4|W_1|_{\max} \\ &= E_g \text{ and } |U| \leqslant |U|_{\max} \\ &\equiv U_{\max} = \frac{1}{2}W_{\max} = \frac{1}{2}E_g, \end{aligned} \tag{5.10}$$

because of the well-known quantum phenomenon of repulsion of close-lying interacting terms[108a] for states generated by two bands (conduction and valence) in the mobility gap. This effect corresponds here to the repulsion of an electronic term, which drops on self-trapping, from the mobility threshold E_v^* of the valence band (and analogously for the hole term) owing to the interband interaction between states in the gap from both bands. [These features and the effect (5.10) were described in Ref. 8 (p.298); see also Refs. 79 and 107.]

Different approaches to the description and analysis of this effect were developed in Refs. 109 and 110 in a study of the Schrödinger equation $\{E_q(x) - [E_q + J_q(x)]\} \cdot \psi_q(x) = \Sigma_p I_{qp}(x)\} \cdot \psi_p(x)$ (see Ref. 108), for which a large part of the matrix elements $I_{qp}(x)$ for transitions between the states ψ_q of "its own" band (for an electron, the conduction band) and ψ_p of the "foreign" band (valance band) are finite owing to the contribution of random fields in the glass, with $\Sigma_p |I_{qp}x) \ll Q_0$ and $|I_q(x)| \lesssim Q_0(J_q(0) \equiv 0 \equiv I_{qp}(0) \equiv I_{qq}(x)$.[2)] Both approaches are apparently limited, though in different respects, and the problem of giving a quantitative description of this effect remains largely open.

For the second case (5.9) we have

$$\begin{aligned} E_g \gg W_{\max} &= |W_2(k=0)| = \varepsilon_g(Q_0) \\ &= 2U_{\max} = 2|U(k=0)|. \end{aligned} \tag{5.11}$$

Thus in the case (5.10) the ST pair states with $U < 0$ are formed only in soft configurations with not too small values of $k \gtrsim k_g \approx Q_0^2 E_g^{-1} \gtrsim k^*$, with $k \lesssim k_l\ (< k^{(0)})$ and in the case (5.11) for any $k \lesssim k_l$. The states (5.3), generally speaking, in the case (5.10) make an appreciable contribution for $\varepsilon_g \approx E_g$, but not for $\varepsilon_g \gg E_g$, while in the case (5.11) there is no repulsion effect, $E_{\max} \ll E_g/2$, so that the situation in these two cases is different.

We note that the ST triplet ($\sigma = 1$) pair states correspond to excitations with a significant energy (per particle) $\varepsilon_{ex}^* \sim U_{\max}/2$ in the gap with $|U(\uparrow\downarrow)| - |U(\uparrow\uparrow)| \sim |U(\uparrow\uparrow)|$; this is analogous to the well-known situation for hydrogen molecules[108] (see Ref. 79). As usual in such cases, when $E_2(\uparrow\uparrow) = E_2(\uparrow\downarrow) + \varepsilon_{ex}^*$, in phenomena involving decay or the formation of similar pairs (recombination, photoluminescence, etc.) effects depending on the value of the spin of the pair can be manifested.

Generally speaking, three basic possible types of electron and hole singlet pairs in ST states, local centers $A^{\mp l}$, with different values of the charge $e^* = \mp l|e|$ can be distinguished: neutral ($l = 0$), singly charged ($l = 1$), and doubly charged ($l = 2$). Such a singlet pair is similar to a weak covalent bond in soft configurations. Thus the weak, "irregular," covalent bond between the ions of the chalcogen ($C^{\pm 1} - C^{\pm 1}$) can play the role of the center $A^{\pm 2}$ in the glassy semiconductors a–$C_{1-x}Q_x$ (see also Ref. 2), while the defects $D^{\pm 1}$ in the model (4.4) can play the role of $A^{\pm 1}$ centers, and the weak covalent bond in the model (4.3) can play the role of A^0. In this sense singlet electron (hole) pairs in the models (4.3) and (4.4) are particular realizations of the ST pairs studied. Apparently the $A^{\pm 2}$ centers make the main contribution, since the concentration of broken bonds is small and local composition fluctuations cause the charged centers to predominate. This is the key to understanding the insensitivity of the properties of such glasses to the injection of a high concentration of hydrogen atoms c_H (~ 0.1), capable of "destroying" the broken bonds, as well as to the solution of some problems of the model (4.4) (see Refs. 65 and 105).

5.2. Density of states. Thermodynamic properties

The density of states of the quasicontinuous spectrum of the system under study in the "mobility" gap per particle is given by

$$g(E) = \sum_n g_n(E), \quad g_n(E) = \sum_{\alpha=1,2} g_n^{(\alpha)}\left(\frac{E_n^{(\alpha)}}{n}\right)_{E_n^{(\alpha)} = nE}, \tag{5.12}$$

where $n = 1$ corresponds to the contribution of single-particle states from the tails of both bands ($\alpha = 1,2$) with $U > 0$, while $n = 2$ corresponds to the ST pair states with $U < 0$.[8,79,104,111] Here $g_n^{(\alpha)}(E)$ is determined by a formula of the type (3.2)—an integral over k and E_q of $g_0^{(\alpha)}(E_q)G(k)\delta(E - E_q + (-1)^\alpha \delta_n^{(\alpha)}(k))$ with $\delta_n^{(\alpha)}(k)n$

$= W_n^{(\alpha)}(k) + U_c^{(\alpha)}\delta_{n,2}$ over the region $E_c^* > E_q > E_v^*$ and in the case (5.10) with $k \gtrsim k_g$, i.e., $|W_2^{(\alpha)}(k)| \lesssim E_q$. The "bare" (in the absence of self-trapping) density of states $g_0^{(\alpha)}(E)$ of this "band" (α) in the mobility gap, generally speaking, includes a slowly decreasing function in the region $E_1^{**} < E < E_c^{**}$ or $E_v^* < E < E_2^{**}$ and a rapidly decreasing function ("tail") of the usual form for $E < E_1^{**}$ and $E > E_2^{**}$ with the typical decay parameter $w_\alpha^* \sim 0.1E_g$ and with the same scale $\delta_\alpha^* \equiv |E_\alpha^{**} - E_\alpha^*|$ (see, for example, Refs. 74, 75, and 122). Here $g_1^{(\alpha)}(E)$ and $g_0^{(\alpha)}(E)$ are qualitatively similar, but the rapid decay of $g_i^{(\alpha)}(E)$ in the gap actually starts below E_α^* by an amount $\sim |W_1^{(\alpha)}|_{\max} \approx \min\{E_g, \varepsilon_g\}/4$.

For glassy semiconductors [the case (5.10)] $g_2^{(\alpha)}(E)$ is determined on the whole by the contribution of the states (5.3), but for realistic values of $E_g \approx \varepsilon_g$ contains also a contribution from the states (5.4). The latter corresponds to the displacement of the density of states near E_α^* into the gap by an amount $(W_{\max}^{(\alpha)} - U_c^{(\alpha)})/2$,

$$g_{(\mathrm{AH})}^{(\alpha)}(E) \approx G(k^*)\, g_0^{(\alpha)}\left[E - \frac{(-1)^\alpha}{2}(W_{\max}^{(\alpha)} - U_c^{(\alpha)})\right]$$

for $W_{\max}^{(\alpha)} = E_g \gg U_c^{(\alpha)}$, and is significant in an interval of width $\approx \max\{U_c;\ \delta^* + w^*\}$ around the center of the gap $\bar{E}$, $E_c^* - \bar{E} = \bar{E} - E_v^* = E_g/2$. The contribution of the states (5.3) $g_{2(\mathrm{H})}^{(\alpha)}(E)$ decreases in the gap like $g_0^{(\alpha)}(E)$ only near E_α^{**} and then deeper than $\bar{E} - (-1)^{(\alpha)}\gamma_\alpha(\Delta_\alpha^* + w_\alpha^*)$ for $\gamma_\alpha \sim 1$. However, it decreases slowly in a significant intermediate region[111]:

$$g_{2\mathrm{AH}}^{(\alpha)}(E) \backsim \left| E_\alpha^* - E + \frac{1}{2}U_c^{(\alpha)}\right|^{-2}. \tag{5.13}$$

In this, main, region of E near $\bar{E}$ $g_{2(\mathrm{H})}(E)$ is determined by two overlapping almost flat bands (5.13), while for $\varepsilon_g \approx E_g$ two "narrower" bands $g_{2(\mathrm{AH})}^{(\alpha)}(E)$ also make a contribution (Fig. 4). In this connection we note that here the symmetry of the characteristics of the electron and hole pairs of states for glassy semiconductors, empirically determined previously and reflected in the region $|U| = E_g/2$, proposed in the model (4.4), is a consequence of (5.10). At the same time $U_{\max}^{(1)} = E_g/2 = U_{\max}^{(2)}$ not only for $Q_0^{(1)} \approx Q_0^{(2)}$, but also for different $Q_0^{(1)}$ and $Q_0^{(2)}$ ($Q_0^{(1)}, Q_0^{(2)} \gtrsim E_g$). The actual redistribution of the electrons accompanying transitions from the filled band $g_2^{(2)}(E)$ of states split off from the tail of the "valence band" (their relative fraction is $f_2 \sim c_a \sim 0.1$) into the empty band $g_2^{(1)}(E)$ of states from the tail of the "conduction band" ($f_1 \sim c_a$), gives rise to the formation of real stable electronic $(2e)_0$ and hole $(2h)_0$ pairs with $\sigma = 0$ and $U < 0$ for effective $|U| = |U|_{\max} = (1/2)E_g$ near $E = \bar{E}$. Their density of states looks like two bands in the quasicontinuous spectrum, joining at the common boundary $E^{(0)} \approx \bar{E}$, with width $\sim\{U_c;\ \delta^* + w^*\} \ll E_g/2$ and height $g_2(E^{(0)}) \approx 10^{19}$–$10^{20}$ $\mathrm{cm}^{-3}\,\mathrm{eV}^{-1}$ ($\sim G(k_y)Q_0^2 w^{*2} a_1^3 \times (E^*)/AU_c^2$), corresponding to a significant concentration of pairs $c_2 \approx a_1^3\, g_2(E^{(0)})E_g/2 \sim fc_t \sim 10^{-2}$–$10^3$; c_t is the relative fraction of states in the "band tails," $c_t \approx 10^{-1} - 10^{-2}$. Pinning $\zeta = E^{(0)} \approx \bar{E}$ (small bias ζ) relative to an increase in the concentration of impurity (non-transition) atoms introduced during vitrification $c_i < 10^{-2}$, the electric field $F \lesssim F^* \approx (1/2)E_g/\ln\,[G(k_y)Q_0^2 w^*/AE_g^2]^{-1} \approx 10^6 - 10^{-7}$ V/cm, or the temperature $T \lesssim T_g/2 \ll T^* \sim |e|a_1 F^* \approx 10^5 - 10^4$ K, is determined by the occupied pair states[8,111]

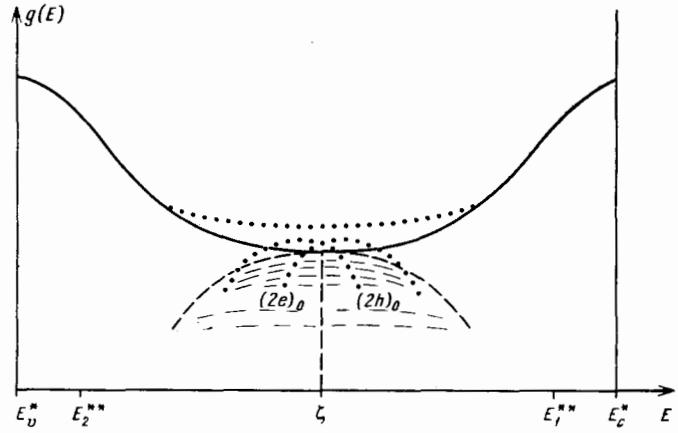

FIG. 4. Schematic form of the density of states $g(E)$ in the mobility gap for a glassy semiconductor. The labels are explained in the text. The bands ("peaks"), bounded by the dashed curve (and partly cross-hatched), correspond to states occupied by electronic $(2e)_0$ and hole $(2h)_0$ pairs. The dotted curve corresponds to the possible behavior of $g(E)$, when the contribution of $g_{2(\mathrm{AH})}(E)$ is noticeable.

$$\zeta - E_v^* = E_c^* - \zeta = \frac{1}{2}E_g$$

$$\text{for } g(\zeta) = g(E^{(0)}) \approx 10^{20} - 10^{19}\ \mathrm{cm}^{-3}\cdot\mathrm{eV}^{-1} \tag{5.14}$$

[compare the model (4.3) as well as the model (4.4) with $g(\zeta) \approx 0$]. Such a system (glassy semiconductor) is for all practical purposes undoped and diamagnetic, since the concentration of EPR centers $c_1 \approx g_1(\zeta)a_1^3 w^*$ is low, $g_1(\zeta) \ll g_2(\zeta)$ and $c_1 \ll c_2$, though finite, in agreement with experiment ($c_1 \lesssim 10^{-6}$; see Refs. 74 and 111).[3)]

For dielectric glasses [the case (5.11)] $g_2(E)$ and c_2 are many orders of magnitude smaller than in semiconductors:

$$c_2 \lesssim \frac{1}{2}g_2(\bar{E})\,a_1^3 E_g \sim (10^{-2} - 10^{-3})\,q_0,$$

$$q_0 \equiv \frac{g_0(|E^* - \nu w^*|)}{g_0(E^*)} \ll 1, \tag{5.15}$$

for example, $q_0 \sim \exp(-\nu) \ll 1$ with $\nu \equiv |(1/2)E_g - |U(k=0)||/w^*$ (for a-SiO_2 it could happen that $\nu \approx 5$–7 for $E_g \approx 9$ eV, $w^* \approx 0.2$–0.3 eV and $|U(k=0)| \approx 3$ eV). At the same time, in agreement with experiment and unlike glassy semiconductors, impurity atoms can make a significant contribution to the electronic properties of such glasses already for quite low concentrations c_i ($\ll 10^{-2}$) in the absence of appreciable pinning $\zeta \approx \bar{E}$ and single-particle states—EPR centers—can play an important role.[57]

5.3. Localized electronic excitations. Weakly nonequilibrium phenomena

In this section we shall discuss primarily the properties of glassy semiconductors, i.e., the case (5.10) and (5.14). The quasicontinuous spectrum of single-particle localized excitations [(1e), (1h)], formed in the decay of ground state ST pairs [$(2e)_0$, $(2h)_0$], has gaps—for thermal (accompanying relaxation of the medium) and optical (without thermal relaxation) processes. The width of the thermal gap is $\varepsilon_{\mathrm{th}} = U_{\max} = 1/2E_g$, while the width of the optical gap is $\varepsilon_{\mathrm{opt}} = U_{\max} + 2|W_1|_{\max} = E_g$ [79,105] (compare Ref. 83). At the same time, taking into account the usual generation of electron-hole (e-h) pairs, the energy of activation of conduction $W_a = \min\{|\zeta - E_\alpha^*|;\ \varepsilon_{\mathrm{th}} + \varepsilon_h\} \approx E_g/2$ (for typical values $w^* \ll E_g$ and the energy of activation of hop-

ping conductivity $\varepsilon_h \ll E_g$), while the total width of the optical gap is $E_{opt} = \min\{\varepsilon_{opt}, E_g\} = E_g$, and the optical absorption edge can be regarded as sharp (see Sec. 4.1) as soon as it is determined by the decay of ST pairs (or creation of *e-h* pairs), while Urbach absorption is determined by the contribution of simple exponential "band" tails (see Ref. 112). This agrees with experiment.

The quasicontinuous spectrum of localized two-particle excitations $[(2e)_{ex}, (2h)_{ex}]$ of ground state ST pairs, unlike the spectrum of possible excitons, does not have a gap [as in the model (4.3) and in the BCS model of a superconductor].[4)] At the same time low-energy excitations with a per particle energy of $\varepsilon_{ex} \ll U_{max}/2 \approx E_g/4$ and high-energy excitations with $\varepsilon_{ex} \gtrsim E_g/4$ can be distinguished. The latter include also the triplet ST pairs $(2e)_{\uparrow\uparrow}$, $(2h)_{\uparrow\uparrow}$ as well as the excitations (1e) and (1h). Electronic excitations associated with soft configurations are generally characterized by metastability. Metastability is manifested most strongly for high-energy excitations, for which restructurings of the atomic bonds correspond to large atomic displacements $|\Delta x| \sim 1$ and, in this sense, the formation of long-lived "defects" (not necessarily reducing to Frenkel or Schottky defects) relative to the starting structure in the glass, in particular, photostructural transformations in glassy semiconductors (see Refs. 74, 113, 114, 115, 120). The elementary act of such defect formation includes a Frank-Condon transition with the absorption of a photon and tunneling transitions or transitions of the Landau-Zener type,[108a] as well as competing thermally activated transitions—decomposition of defects. Analysis of the probability $P(\omega,T)$ and other characteristics of the formation of defects, induced by the absorption of a photon with energy $\hbar\omega \approx E_g$, leads to a number of preliminary results, of which we call attention to the following.

The probability $P(\omega,T)$ is highest at $T = 0$, and as T rises it decreases monotonically for high $\hbar\omega \gtrsim \bar{E}_g^{**} \times (\hbar\omega \approx E_g)$. On the other hand, $P(\omega,T=0) = 0$ for lower energies $\hbar\omega < \bar{E}_g^{*}(\hbar\omega \approx E_g)$ or $P(\omega,T=0)$ for intermediate values of ω, $\bar{E}_g^{*} \lesssim \hbar\omega \lesssim \bar{E}_g^{**}$; at the same time $P(\omega,T)$ varies nonmonotonically as T increases, increasing at first and then, owing to annealing at $T_g \gtrsim T \gtrsim T_{ann}$, decreases (Fig. 5). For $\hbar\omega \gtrsim \bar{E}_g^{**}$ the process, i.e., $P(\omega,T)$, is virtually independent of ω (the plateau at $T = \text{const}$). The threshold energies $\bar{E}_g^{*}$ and $\bar{E}_g^{**}$ are the average values of the characteristics $\bar{E}_g^{*}$ and $\bar{E}_g^{**}$, averaged over the ensemble of soft configurations, of the adiabatic potential of the system, corresponding to the transitions of interest; its barriers cause the metastability of the excitations and "defects" (Fig. 6). At the same time $\bar{E}_g^{*} < \bar{E}_g^{**} \lesssim E_g$ and $\bar{E}_g^{*} \approx \bar{E}_g^{**} \approx E_g$.

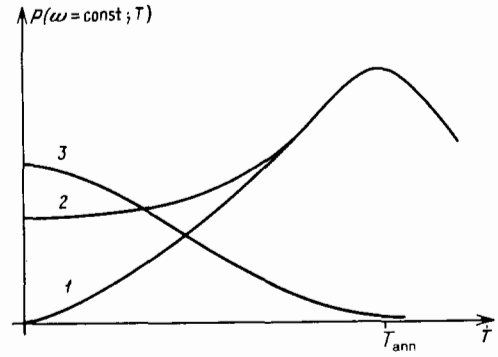

FIG. 5. Schematic form of the possible types of dependences $P(\omega = \text{const}; T)$; T_{ann} is the effective temperature of annealing. (1): $\hbar\omega < \bar{E}_g^{*}$, (2) $\bar{E}_g^{*} \geqslant \hbar\omega < \bar{E}_g^{**}$, (3) $\hbar\omega \geqslant \bar{E}_g^{**}$.

Furthermore, the sign and magnitude of the change in the volume (thickness of the film) of the glass, $\Delta\Omega(\omega) \equiv \Omega(\omega) - \Omega$, in these processes depends on the magnitude of the ratio $\gamma_{12} \equiv p_1(\omega)c_2/p_2(\omega)c_a^{*}$, where $p_1(\omega)c_2$ corresponds to the decay of electron (hole) pairs with the absorption of a photon, while $p_2(\omega)c_a^{*}$ corresponds to the formation of new pairs. For $\gamma_{12} > 1$ the chemical bonds corresponding to such pairs become weaker, and "photoexpansion," $\Delta\Omega(\omega) > 0$ occurs. At the same time the number of two-well atomic potentials and tunneling TLS in them as well as anomalies caused by them in the heat capacity $C(T)$ ($\propto T$) and other characteristics at temperatures $T \lesssim 1$ K increase. This occurs most likely for $\hbar\omega < \bar{E}_g^{*}$ and $\hbar\omega \approx E_g$. The opposite occurs with $\Delta\Omega(\omega) < 0$ and $\Delta C(T) < 0$ for $T \lesssim 1$ K, when $\gamma_{12} < 1$; this can be realized for $\hbar\omega > \bar{E}_g^{**}$ and $\hbar\omega \approx E_g$, when the created electron-hole pairs populate soft configurations with the formation of new electron (hole) pairs. This situation with $\Delta C(T) < 0$ for $T \lesssim 1$ K and $\hbar\omega \approx E_{opt}$ was apparently recently observed in a-As_2S_3.[116]

Such effects are one of the manifestations of the general relationship between anomalous low-energy excitations and electronic localized states, generated by soft configurations, in glassy semiconductors.[65] The photostructural transformations under discussion lead, in particular, to the appearance of localized electronic states, so that the optical gap should decrease $|\Delta E_{opt}(\omega)|$, and its decrease $|\Delta E_{opt}(\omega)|$ should increase with ω up to the "plateau," $|\Delta E_{opt}|_{max} \ll E_g/2$ for $\hbar\omega > \bar{E}_g^{**}$, in agreement with experiment.[114,115] The existence of long-lived excitations and structural changes determined by them corresponds to the existence of their slow relaxation over a long time. The latter is charac-

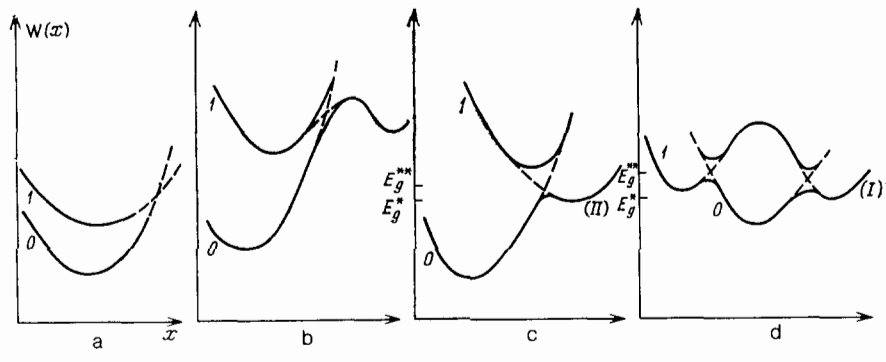

FIG. 6. Typical adiabatic potentials of the ground (0) and excited (1) states of the soft configuration. In the cases of Figs. b and c the separated bottom branch (I) corresponds to a two-well potential, while in the case of Fig. d it corresponds to a three-well potential with strongly nonequivalent central and side wells.

terized by a macroscopic time scale ($\gtrsim 10^3$ s) and is also manifested in other phenomena, in particular, in photoconductivity (see Ref. 121).

Here two classes of possible centers of photoluminescence (PL) can be distinguished.[65,79,105]

I. High-energy excitations $(2e)^*_{ex} \equiv \{(1e)^* + e^*\}$ and $(2h)^*_{ex} \equiv \{(1h)^* + h^*\}$, in which the state of one of the charge carriers (e^*, h^*) is less strongly localized ($\rho^* \gg a_1$) than the state of the other $[(1e)^*, (1h)^*]$.

II. ST excitons, $\{(1e)^* + h^*\}$, $\{(1h)^* + e^*\}$, with a similar structure. The energy of the PL peaks $E^{(l)}_{PL}$ $(1 \leqslant l \leqslant l_0)$, in the presence of l_0 types of centers $(1 \leqslant l_0 \leqslant 4)$, are close, $E^{(l)}_{PL} \approx E_g/2$, and their differences are comparable to the widths of the peaks $\sim [E_g \hbar (2k_g/M)^{1/2}]^{1/2} \sim 0.1$ eV; one or several PL bands can be distinguished. The threshold energy for excitation of PL $E^{(II)}_X(PL) = E_{opt}$, but is somewhat lower for the I centers, $0 < E_{opt} - E^{(I)}_X(PL) \lesssim 0.1 E_{opt}$, and the latter can determine the significant PL, observed in glassy semiconductors for $E_{opt} - \hbar\omega \approx 0.1 E_{opt}$ and whose kinetics is monomolecular.[102] The total Stokes shift is very large, $E_X(PL) - E_{PL} = E_g/2$, which also agrees with experiment.[102] The fading of PL is determined here by the photo- structural transformations of PL centers in centers of competing nonradiative processes, depending weakly on T. As the pressure p (density $\bar{\rho}_a$) increases the behavior of the PL can differ for centers I and II: $E^{(II)}_{PL}(p)$ can vary nonmonotonically, with a section of growth, while $E^{(I)}_{PL}(p)$ decreases monotonically[49]; comparison with experiment[117] could make it possible to separate the contributions of the centers (1) and (2) in PL in glassy semiconductors.

Thermal quenching of PL (4.2) is determined here both by the decrease of the probability of a radiative transition $p_r(T)$ owing to the emission of vibrational excitations with energy $\mathscr{E}^* \approx 20$–40 K as T increases (analog of the decay of the zero-phonon absorption line; see Ref. 62) and by the growth in the probability p_r of nonradiative decay of PL centers.[95] Taking into account the latter with specific, different in different models,[94–96,118] assumptions can lead to the law (4.2) in a limited range of values of the parameters of the system. Taking into account the first factor $p_r(T)$, however, naturally leads to the law (4.2) with $I_{PL} \propto p_r(p_r + p_{nr})^{-1} \propto \exp(-T/T_A)$ for $T > T'_A \approx T_A \approx \mathscr{E}^* \approx w \approx 10$–$30$ K, as soon as the temperature dependence of p_{nr} is weaker (like PL fading, see above) and $p_{nr} \gg p_r$. In the model under discussion the emitted excitations are the excitations (3.23), which interact with the weakly bound charge carrier in the PL center[52,119] (compare Ref. 60, where interlayer optical vibrations can play a similar role). Apparently there is still no general quantitative theory of the law (4.2).

In the theory under discussion the high-energy electronic excitations—local charged (or neutral) centers for different nonequilibrium phenomena in glassy semiconductors—are also different. This makes it possible to understand, at least qualitatively, the empirically observed differences in the magnitudes and ω and T dependences, which are difficult to interpret in the models (4.3) and (4.4), of the cross sections of the correlated photo-EPR, intragap absorption (with characteristic energy $E_{IA} \approx E_g/2$), PL fading,[74,101] and the significant increase in the number of hole trapping centers accompanying a weak change in other effects as the number of donors (Tl) increases, $c_1 \approx 10^{-6}$–10^{-2} ($\lesssim c_2$),[100] since the excitations (1e) and (1h) make a different contribution to all these phenomena.[65,105]

The relations obtained in this theory in the case (5.10) and (5.14) for glassy semiconductors[8,79]

$$E_{opt} = 2E_{IA} = 2W_a = 2E_{PL} = E_x(PL) = E_g \quad (5.16)$$

describe the empirically observed correlations between these phenomena (see Secs. 4.1 and 4.2), i.e. (see also Refs. 8, 79, 110, 121) effective discrete energies against the background of the quasicontinuous spectrum (compare Refs. 74 and 77).

For dielectric glasses in the case (5.11) many of these phenomena are much weaker (see the end of Sec. 5.2).

Finally, the low-energy excitations of ST pairs can contribute to the heat capactiy ($C_e \propto T$), and to the aggregate of tunneling TLS (see Refs. 2 and 77) and the phenomena determined by them ($\sigma'(\omega) \propto \omega$ etc.) at low temperatures $T \lesssim 1$ K in glassy semiconductors. The question of the importance of this contribution remains largely open (see Refs. 84 and 93).

5.4. Concluding remarks

The foregoing theory of localized electronic states in glasses makes it possible to describe in a unified manner the properties of glassy semiconductors determined by these states as well as their correlation with one another and with the low-temperature properties of such glasses; this is determined by their common origin in soft atomic configurations. The fundamental role of the latter and ST states in them is determined by the "nonbinding" orbitals (unshared pairs, etc.) and weak "irregular chemical bonds" (of the type Se-Se in a-As_2Se_3), in agreement with the experimental data for glassy semiconductors.[74] The models (4.3) and (4.4) can be regarded in some sense as particular realizations of the theory discussed here, on the basis of which the problems mentioned in Secs. 4.2 and 4.3 can also be solved. A number of problems of the foregoing theory concern its quantitative aspects, as well as the effects of interactions between electron pairs and their role in the superconductivity of glassy semiconductors (see Ref. 123).

6. CONCLUSIONS

In this review some recently developed theoretical ideas and a theory, based on them, of anomalous low-energy (nonphonon) excitations and localized electronic states with strong interelectronic interaction and anomalous phenomena in glasses due to them, and, as a rule, absent in crystals, were discussed. They are determined by the significant anharmonicity of the crystal, regarded as a heterogeneous structure: soft configurations of weakly bound atoms, whose relative fraction is significant $c_a \sim 0.1$ and which correspond to significant fluctuations away from short-range order (and stoichiometry) and, generally speaking, excess (compared with a crystal) volume, are "dissolved" in a random manner in the main aggregate of the usual local atomic configurations. In this connection the theory predicts that the density of states of both the low-energy excitations and the self-trapped electron pairs with $U < 0$ should decrease [see (5.15)] and that the corresponding properties of the glass will become weaker as the density of the glass increases (high pressures, annealing, etc.)[8] (see also Ref. 48). The

idea of a "point defect" in the structure of the glass does not appear unique here (see also Refs. 2, 34, 74, and 105): the soft configurations (3.1) and $A^{\pm l}$ centers, though they can be regarded as local centers, are an important component of the characteristic structure of the glass.[5),132]

I had an invaluable opportunity to discuss a number of problems in the theory of glassy systems with I. M. Lifshitz. I thank Yu. M. Kagan, M. I. Kaganov, M. A. Krivoglaz, L. P. Pitaevskiĭ, M. I. Ryazanov, and I. I. Yaskovets for useful discussions of some questions examined in this review, and also S. Hunklinger, who provided me with reprints of Refs. 31, 32 and Refs. 125–127, and K. Tanaka for providing me with a preprint of Ref. 128.

[1)]The phenomena determined by the participation of conduction electrons (electronic excitations) are discussed in detail in some recent reviews (see, for example, Refs. 3, 12, and 31).

[2)]The almost linear, far from $E^*_{v,c}$, decrease in the term $J_q(x) = -\alpha_q|x|$ in the gap slows down and the states of both bands mix appreciably, $\psi_q(x) = c_q(x)\psi_q + \Sigma_p c_{qp}(x)\psi_p$ for $\Sigma_p|c_{qp}(x)|^2 \sim |c_q(x)|^2$, for sufficiently large $|x|$. At the same time the term of the ST pair state $E_q(x_2)$, being repelled, stops near $E^*_{v,c}$: $E_q(x_2) = E^*_{v,c} \pm \Delta_q$ with $|J_q(x_2)| \approx E_g - \Delta_q$, $0 \leqslant \Delta_q \ll E_g/2$ and $\Delta_q \sim (\Sigma_p|I_{qp}(x^*)|^2)^{1/2}$ for $E_q(x^*) = E^*_{v,c}$. Consequently, $W_{max} \equiv |W_2(k_g)| = E_g(1-\delta)$ for $\delta \equiv (\Delta_q)_{cp}/E_g \ll 1$.

[3)]As the density of the material increases (at high pressure, with annealing, etc.) $c_2, g_2(E)$, and $g_2(\zeta)$ decrease together with $c_a(\bar{\rho}_a)$ [see discussion below (3.10)], and hence the pinning ζ and the phenomena discussed below, determined by centers with $U<0$, become weaker.

[4)]Optical excitation and migration (conductivity) of ST pairs as a whole can be neglected here, in agreement with the model (4.3).

[5)]After this paper was submitted for publication, the new publications Refs. 124–129, concerning separate questions discussed in this review, appeared. In Ref. 124 it is pointed out that together with the case $F_0^* \equiv F(0,\bar{\xi}) \neq 0$ the alternative case $F_0^* = 0$, when in contrast to (3.24) the density of states of quasiharmonic excitations can have the form $n_{HV}(\mathscr{E}) \sim \omega^4$ in the region $\hbar\omega_D \gg \mathscr{E} = \hbar\omega \gg w$, is also possible. Interesting experimental studies of the absorption of low-frequency sound in metallic glasses are described in Ref. 125; their interpretation in this article can also have a bearing on the foregoing in connection with (3.27). The model of Ref. 129 can be regarded as a definite realization of the general model (3.1)–(3.3) and (3.11)–(3.14) (see Fig. 3) with the rotational critical mode in (3.1). In the recent paper of Ref. 131 a general theory of the relaxation of TLS in an amorphous metal is developed taking into account the electronic polaron effect with tunneling, and an interpretation is proposed for the anomalous absorption of sound, found in Ref. 125, accompanying the transition of the metal into the superconducting state.

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